

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平11-229185

(43) 公開日 平成11年(1999) 8月24日

(51) Int.Cl.⁸
 C 2 5 D 11/04
 11/18
 // H 0 1 L 21/02
 21/203
 21/205

識別記号
 3 0 2
 3 0 1

F I
 C 2 5 D 11/04 3 0 2
 11/18 3 0 1 Z
 H 0 1 L 21/02 Z
 21/203 Z
 21/205

審査請求 未請求 請求項の数 7 O L (全 9 頁) 最終頁に続く

(21) 出願番号 特願平10-31254

(22) 出願日 平成10年(1998) 2月13日

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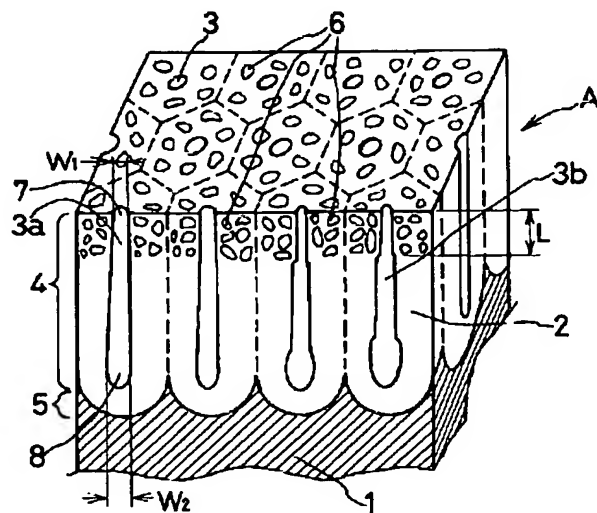
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(54) 【発明の名称】 耐熱割れ性および耐食性に優れた A 1 材料

(57) 【要約】

【課題】 高温熱サイクル下で、ガスやプラズマの腐食環境下にあっても、陽極酸化皮膜に割れが発生せず、しかもガスやプラズマに対する耐食性に優れた陽極酸化皮膜を設けた Al 合金材料を提供する。

【解決手段】 耐熱割れ性および耐食性に優れた Al 材料として、ポアを有するポーラス層 4 とポアのないバリア層 5 とを有する陽極酸化皮膜 A が表面に形成された Al 材料であって、前記ポーラス層 4 のポア 3 の径を、Al 合金基材側 w_2 に比して陽極酸化皮膜の表面側 w_1 を小さくし、かつ皮膜中にペーナイトおよび/ または擬ペーナイト 6 が形成されていることである。



【特許請求の範囲】

【請求項1】 ポアを有するポーラス層とポアのないバリア層とを有する陽極酸化皮膜が表面に形成されたAl材料であって、前記ポーラス層のポア径を、Al合金基材側に比して陽極酸化皮膜の表面側を小さくし、更に、陽極酸化皮膜表面から皮膜厚さの5%以上の深さ部分で、かつ皮膜層に対する体積率で20%以上の部分がベーマイトおよび/または擬ベーマイトを形成していることを特徴とする耐熱割れ性および耐食性に優れたAl材料。

【請求項2】 前記陽極酸化皮膜表面から皮膜厚さの90%以下の深さ部分で、かつ皮膜層に対する体積率で80%以下の部分がベーマイトおよび/または擬ベーマイトを形成している請求項1に記載の耐熱割れ性および耐食性に優れたAl材料。

【請求項3】 前記陽極酸化皮膜が、C、S、N、P、F、Bの内から選択された1種または2種以上の元素を0.1%以上含有する請求項1または2に記載の耐熱割れ性および耐食性に優れたAl材料。

【請求項4】 前記ポーラス層のポア径が、深さ方向の任意区間で非連続的な変化部を有している請求項1乃至3のいずれか1項に記載の耐熱割れ性および耐食性に優れたAl材料。

【請求項5】 前記ポーラス層のポア径が、深さ方向の任意区間で連続的な変化部を有している請求項1乃至4のいずれか1項に記載の耐熱割れ性および耐食性に優れたAl材料。

【請求項6】 前記Al材料が、真空容器またはプロセス反応容器用である請求項1乃至5のいずれか1項に記載の耐熱割れ性および耐食性に優れたAl材料。

【請求項7】 前記真空容器またはプロセス反応容器が、半導体または液晶の製造装置用である請求項1乃至6のいずれか1項に記載の耐熱割れ性および耐食性に優れたAl材料。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、Al合金表面に陽極酸化皮膜を形成したAl材料に関し、特に高温腐食環境下での耐熱割れ性および耐ガスあるいは耐プラズマの耐食性に優れた材料として、半導体や液晶の製造装置などの真空容器用に適するAl材料に関するものである。

【0002】

【従来の技術】CVDやPVDなどの化学的或いは物理的真空蒸着装置、またはドライエッチング装置などの半導体や液晶の製造装置は、ヒーターブロック、チャンバー、ライナー、真空チャック、静電チャック、クランプ、ベローズ、ベローズカバー、サセプタ、ガス拡散板、電極などの主要部材から構成される。これら半導体や液晶の製造装置の内部には、反応ガスとしてClやF、Brなどのハロゲン元素や、O、N、H、B、S、Cなどの元素を含む腐食性のガスが導入されるため、これらの主要部

材には、前記腐食性のガスに対する耐食性（ガス耐食性）が要求される。また、これらの主要部材には、前記腐食性のガスに加えて、ハロゲン系のプラズマも発生するので、このプラズマに対する耐食性が要求される。

【0003】従来から、この種材料としては、ステンレス鋼が用いられてきた。しかし、近年の半導体や液晶の製造装置の高効率化や軽量化の要求に伴い、ステンレス鋼を使用した部材では、熱伝導性が不十分で装置作動時に時間を要する、また重量も大きく装置全体が重量化することなどが問題になっている。しかも、ステンレス鋼に含まれるNiやCrなどの重金属が何らかの要因でプロセス中に放出されて汚染源となり、半導体や液晶の製品の品質を劣化させるという問題もある。

【0004】このため、このステンレス鋼に代えて、軽量で、熱伝導性が高いアルミニウム（以下、Alと言う）合金の使用が急増している。このAl合金の中でも、Mn:1.0~1.5%-Cu:0.05~0.20%などを含むJIS 3003Al合金、Mg:2.2~2.8%-Cr:0.15~0.35%などを含むJIS 5052Al合金、Cu:0.15~0.40%-Mg:0.8~1.2%-Cr:0.04~0.35%などを含むJIS 6061Al合金等が、汎用的に用いられている。しかし、これらAl合金表面は、前記腐食性のガスやプラズマに対して耐食性が優れる訳ではない。したがって、Al合金を半導体や液晶の製造装置などの真空容器用の材料として適用するためには、このガスやプラズマに対する耐食性を改善することが必須の条件となる。そして、Al合金のガスやプラズマに対する耐食性を改善するためには、Al合金表面に何らかの表面処理を施すことが最も有効な手段となる。

【0005】そこで、真空チャンバ部材などのガスやプラズマに対する耐食性を上げるために、耐食性に優れた陽極酸化(Al_2O_3)皮膜を、前記Al合金表面に形成する技術が、特公平5-53870号で提案されている。ただ、この陽極酸化皮膜も、皮膜の膜質によって、前記ガスやプラズマに対する耐食性が大きく異なるため、半導体製造装置部材としての使用環境によっては、これら耐食性の要求を満足することができない。

【0006】このため、半導体製造装置などの部材としてのAl合金の耐食性を改善する目的で、陽極酸化皮膜の膜質を更に向上させる試みも種々提案されている。例えば、特開平8-144088号公報では、陽極酸化皮膜を形成する際、陽極酸化の初期電圧より終期電圧を高くすることが提案されている。また、特開平8-144089号公報では、硫酸やリン酸イオンを含む溶液中で陽極酸化処理を行い、陽極酸化皮膜表面の凹部を特定の範囲とすることが提案されている。更に、特開平8-260195号や特開平8-260196号公報では、まずポーラス型陽極酸化処理を施し、次いで非ポーラス型陽極酸化処理を施すことが提案されている。

【0007】これら陽極酸化処理に関する従来技術は、いずれも、図2に示す通り、基材Al合金1の表面に、電

解開始とともにポア3 と呼ばれる凹部（孔）を形成しながらAl合金1 の深さ方向に成長するセル2 からなるポーラス層4 と、ポアの無いバリア層5 からなる陽極酸化皮膜B を設けることを基本としている。このような、通常の陽極酸化皮膜においては、図2 のように、ポア3 の径は、陽極酸化皮膜の表面側とAl合金基材側で同一となる。そして、このような陽極酸化皮膜構造においては、ポアの無いバリア層5 がガス透過性を有しないからガスやプラズマが、Al合金1 と接触するのを防止している。また、特開平8-193295号公報などでは、この2重構造の陽極酸化皮膜のプラズマに対する耐食性を更に向上させるため、ポーラス層4 の表面側のポア径やセル径をできるだけ小さくすることが提案されている。

【0008】

【発明が解決しようとする課題】前記ポアを多数有するポーラス層とポアの無いバリア層とを有し、ポーラス層4 の表面側のポア径をやセル径でできるだけ小さくする陽極酸化皮膜は、確かに、前記ガスやプラズマに対する耐食性に優れる。しかし、半導体や液晶の製造条件は、最近の高効率化や大型化により、非常に厳しいものとなっており、ガス、プラズマ条件もより高濃度、高密度、高温化している。したがって、その反応容器（チャンバー）の構成部材や内部での使用部材に対しては、ClやF、Brなどのハロゲン元素や、O、N、H、B、S、Cなどの元素を含む腐食性のガスやプラズマに対する耐食性が必要であり、その要求は近年益々厳しくなっている。これに対し、前記陽極酸化処理によって得られる陽極酸化皮膜では、この厳しくなっている前記ガスやプラズマに対する耐食性の要求に答えられない。

【0009】また、一方で、本発明が対象とする半導体の製造装置用材料に対する耐熱性の要求（課題）も、近年益々厳しくなっている。特に、半導体の製造装置用部材では、半導体の製造のプロセス条件により、前記した通り、使用中に高温域での熱サイクルを数多く受けるといった厳しい使用環境下にある。このため、前記陽極酸化処理によって得られる陽極酸化皮膜は、この高温熱サイクル下では、陽極酸化皮膜に割れが発生し、前記ガスやプラズマの腐食環境下においては、この陽極酸化皮膜の割れから腐食成分が侵入して、基材であるAl合金を腐食させるという問題がある。したがって、これら半導体の製造装置用材料に対する耐熱性の要求を満たすためには、高温熱サイクル下での陽極酸化皮膜の割れ発生を防止した、耐熱割れ性を改善する必要がある。

【0010】本発明はこの様な事情に着目してなされたものであって、その目的は、高温熱サイクル下で、しかも、前記ガスやプラズマの腐食環境下にあっても、陽極酸化皮膜に割れが発生せず、しかも前記ガスやプラズマに対する耐食性により優れる陽極酸化皮膜を設けたAl合金、即ち真空容器用などのAl材料を提供しようとするものである。

【0011】

【課題を解決するための手段】この目的を達成するため、本発明の要旨は、耐熱割れ性および耐食性に優れたAl材料として、ポアを有するポーラス層とポアのないバリア層とを有する陽極酸化皮膜が表面に形成されたAl材料であって、前記ポーラス層のポア径を、Al合金基材側に比して陽極酸化皮膜の表面側を小さくし、更に、陽極酸化皮膜表面から皮膜厚さの5%以上の深さ部分で、かつ皮膜層に対する体積率で20%以上の部分がベーマイトおよび/または擬ベーマイトを形成していることである。

【0012】陽極酸化皮膜の表面或いは全体を、ベーマイトおよび/または擬ベーマイトにより封孔すること自体は周知である。即ち、陽極酸化皮膜を設けたAl合金材料を、温水、加圧水、水蒸気等により処理し、陽極酸化皮膜の表面或いは全体を、ベーマイト化あるいは擬ベーマイト化して、陽極酸化皮膜のポーラス層のポアを封孔して、陽極酸化皮膜の耐食性をより向上させることは周知である。

【0013】しかし、これら従来周知の封孔処理の目的は、陽極酸化皮膜を設けたAl合金材料の湿潤乃至塩類等が存在する雰囲気や大気下での、一般的な腐食環境下における耐食性をより向上させるためのものである。したがって、本発明のような、高温熱サイクル下で、しかも、前記ガスやプラズマの腐食環境下での陽極酸化皮膜を設けたAl合金材料の陽極酸化皮膜の割れ防止や、ガスやプラズマに対する耐食性の向上目的ではない。

【0014】しかも、封孔の対象とする陽極酸化皮膜を設けたAl合金材料も、陽極酸化皮膜のポーラス層のポアの径が、陽極酸化皮膜の表面側とAl合金基材側で同一となる通常の陽極酸化皮膜構造のものを対象としており、本発明のような、ポーラス層のポア径を、Al合金基材側に比して陽極酸化皮膜の表面側を小さくした、傾斜構造乃至多層構造の陽極酸化皮膜構造のものを対象とするものではない。

【0015】そして、これら従来周知の封孔処理は、ポーラス層のポアを完全に封孔することを目的として、陽極酸化皮膜全体を、ベーマイト化あるいは擬ベーマイト化する。このため、ベーマイト化あるいは擬ベーマイト化した陽極酸化皮膜の体積が大きく変化（膨張）する。したがって、前記真空容器またはプロセス反応容器用のような、Al材料の使用環境や条件によっては、陽極酸化皮膜の深さ方向に割れが発生し、陽極酸化皮膜の耐熱割れ性や耐蝕性が却って劣化する。特に、前記高温熱サイクル下で、しかも、前記ガスやプラズマの腐食環境下では、その傾向が著しく使用に耐えないものとなる。

【0016】このような従来の封孔処理における、陽極酸化皮膜の前記体積変化に伴う割れを防止するためには、前記高温熱サイクル下で、しかも、前記ガスやプラズマの腐食環境下にあっても、この環境で生じる陽極酸化皮膜とAl合金基材間の熱応力差、および陽極酸化皮膜

内部に発生する応力を緩和（緩衝）することが必要となる。このため、本発明では、前記ポーラス層のボア径を、Al合金基材側に比して陽極酸化皮膜の表面側を小さくし（陽極酸化皮膜の表面側で小さく、かつAl合金基材側で大きくしてなるようにし）、陽極酸化皮膜を多層構造または傾斜構造とする。そして、陽極酸化皮膜のペーマイト化あるいは擬ペーマイト化量を、陽極酸化皮膜の割れ防止と耐蝕性の観点から、特定の範囲とする。

【0017】即ち、本発明における陽極酸化皮膜のペーマイト化あるいは擬ペーマイト化量は、好ましくは、前記高温熱サイクル下で、しかも、前記ガスやプラズマの腐食環境下にあっても、耐食性を向上させるためにボアを封孔するための必要量以上とするが、この環境で生じる陽極酸化皮膜とAl合金基材間の熱応力差、および陽極酸化皮膜内部に発生する応力の程度により、陽極酸化皮膜の割れが生じるような量以下とする。また、前記ポーラス層のボア径を、Al合金基材側に比して陽極酸化皮膜の表面側を小さくする程度も、この環境で生じる陽極酸化皮膜とAl合金基材間の熱応力差、および陽極酸化皮膜内部に発生する応力の程度と、これらを緩和して、陽極酸化皮膜の割れを防止できる効果を実質的に達成できるものとするが、本発明の基本的な考え方である。

【0018】なお、本発明のペーマイトあるいは擬ペーマイトの形成によって、ボアが結果的に封孔される場合があるが、本発明では、その封孔の程度（完全封孔、半封孔）が問題ではなく、あくまで、形成されるペーマイトあるいは擬ペーマイトの量が、目的とする耐熱割れ性および耐食性を支配するものである。

【0019】

【発明の実施の形態】この基本的な考え方にもとづく、本発明の陽極酸化皮膜構造を図1に模式的に示す。この図1に示す通り、本発明の陽極酸化皮膜Aは、基材Al合金1の表面に、ボア3を有し、Al合金1の深さ方向に成長するセル2からなるポーラス層4と、ボアの無いバリア層5からなる。そして、ボア3は、陽極酸化皮膜の表面側のボア径 w_1 を、Al合金基材側のボア径 w_2 よりも小さくし、このボア径の変化が、ボア3aのように深さ方向の任意区間で連続的な変化部を有していても、また、ボア3bのように深さ方向の任意区間で非連続的な変化部を有していても、或いはこれらが混在していても構わない。本発明では、ボア径が連続的な変化部を有しているボア3aの場合を前記傾斜構造と言い、ボア径が非連続的な変化部を有しているボア3bの場合を前記多層構造と言う。なお、通常の陽極酸化皮膜においては、前記した図2のように、ボア3の径は、陽極酸化皮膜の表面側とAl合金基材側で同一となる。

【0020】そして、このような陽極酸化皮膜Aにおいて、更に、ペーマイトおよび/または擬ペーマイト6を、陽極酸化皮膜表面から皮膜厚さの5%以上、好ましくは90%以下の皮膜深さ（厚さ）1の部分に、皮膜層に対す

る体積率で20%以上、好ましくは80%以下含有させて、陽極酸化皮膜の表面層を部分的にペーマイト化あるいは擬ペーマイト化させる。この場合、ペーマイト化あるいは擬ペーマイト化させるのは、主として陽極酸化皮膜のポーラス層4であるが、皮膜条件によっては、バリア層に至ることもある。

【0021】本発明で言うペーマイトあるいは擬ペーマイトは、Alの水和酸化物であり、一般式、 $Al_2O_3 \cdot xH_2O$ で表され、水和処理により、陽極酸化皮膜のAlの酸化物の水和反応により生成したAlの水和酸化物を言う。そして、前記Xの値が約1～1.9のものをペーマイト若しくは擬ペーマイトと一般的に称されている。

【0022】この陽極酸化皮膜中のペーマイトあるいは擬ペーマイトの量の測定は、例えば、2万倍以上の走査型電子顕微鏡による形態的な観察だけでは、特に形成しているペーマイトあるいは擬ペーマイトが微細な結晶の場合に難しい。したがって、ペーマイトあるいは擬ペーマイトの量の測定は、X線回折、X線光電子分光分析(XPS)、赤外線分光分析法(FT-IR)などを用いることにより、正確に測定することができる。例えば、FT-IRの場合を例にとると、 $3000 \sim 3700 cm^{-1}$ 付近に認められるAl-O \leftrightarrow Hの伸縮振動による吸収スペクトル、および $1050 \sim 1100 cm^{-1}$ 付近に認められるAl-O \leftrightarrow OHの伸縮振動による吸収スペクトルの、いずれか一つが認められることにより、Alの水和酸化物皮膜の存在が確認され、それらのスペクトルの強度から、元の陽極酸化皮膜の非晶質な組織との識別および陽極酸化皮膜の深さ（厚み）方向の定量的な分析が可能である。また、X線回折では、Al-OOHのX線回折ピーク強度から、同様に定量的な分析が可能である。

【0023】次に、ペーマイト化あるいは擬ペーマイト化の本発明での量的な条件について説明する。まず、本発明では、前記ガスやプラズマの腐食環境下での、耐食性を向上させるため、陽極酸化皮膜のペーマイトあるいは擬ペーマイト形成量を、ペーマイトあるいは擬ペーマイトが、陽極酸化皮膜表面から皮膜厚さの5%以上の深さに、好ましくは40%以上の深さに、かつ皮膜層に対する体積率で20%以上、好ましくは50%以上含有させる。

【0024】なお、ペーマイトと擬ペーマイトの機能（効果）は同じであり、陽極酸化皮膜中に形成乃至含有させるのは、ペーマイトあるいは擬ペーマイトの単独であっても、混合であっても良い。

【0025】ペーマイトあるいは擬ペーマイトが含有される陽極酸化皮膜の厚さが、皮膜厚さの5%未満であれば、ガスやプラズマに対する耐食性が十分ではなくなる。また、陽極酸化皮膜の当該表面部分の、ペーマイトあるいは擬ペーマイトの含有量が、皮膜層に対する体積率で20%未満の場合にも、ガスやプラズマに対する耐食性が十分ではなくなる。

【0026】一方、本発明では、前記高温熱サイクル下

およびガスやプラズマの腐食環境下で生じる、陽極酸化皮膜とAl合金基材間の熱応力差や陽極酸化皮膜内部に発生する応力により、陽極酸化皮膜に割れが生じることを防止するために、ペーマイトあるいは擬ペーマイトが含有される陽極酸化皮膜の厚さ（深さ）の上限を、皮膜厚さの90%以下、また、陽極酸化皮膜の当該表面部分の、ペーマイトあるいは擬ペーマイトの含有量の上限を、皮膜層に対する体積率で80%以下とすることが好ましい。

【0027】本発明の要件の一つである、ポア径をAl合金基材側に比して陽極酸化皮膜の表面側を小さくする陽極酸化皮膜の多層構造化や傾斜構造化により、前記熱応力差や応力は緩和され、陽極酸化皮膜に割れが生じることを基本的に防止できる。しかし、Al合金材料の使用環境がより厳しくなる際の、陽極酸化皮膜の割れをより確実に防止するためには、前記陽極酸化皮膜のペーマイト化あるいは擬ペーマイト化の好ましい上限の条件が必要となる。

【0028】即ち、ペーマイトあるいは擬ペーマイトが含有される陽極酸化皮膜の厚さが、皮膜厚さの90%を越えると、また、陽極酸化皮膜の当該表面部分の、ペーマイトあるいは擬ペーマイトの含有量が、皮膜層に対する体積率で80%を越えると、前記従来の封孔処理と同様に、陽極酸化皮膜の実質的に皮膜全体が、前記ペーマイト化あるいは擬ペーマイト化することになり、陽極酸化皮膜の体積の変化（膨張）がより大きくなる。このため、陽極酸化皮膜の深さ方向に割れが発生しやすくなり、前記Al合金材料の使用環境がより厳しくなる際には、陽極酸化皮膜の割れ性や耐蝕性が却って劣化する結果となってしまいう可能性があるからである。

【0029】次に、前記した通り、ポーラス層とバリア層を有する陽極酸化皮膜において、陽極酸化皮膜の体積変化に伴う割れを防止するためには、陽極酸化皮膜自体が、前記高温熱サイクル下で、しかも、前記ガスやプラズマの腐食環境下でも、この環境で生じる陽極酸化皮膜とAl合金基材間の熱応力差、および陽極酸化皮膜内部に発生する応力を緩和（緩衝）できる構造であることが必要となる。このための陽極酸化皮膜構造自体の改善として、本発明では、ポーラス層の表面側のポア径を、Al合金基材側に比して小さくすることを選択している。この他の態様として、ポア径をポーラス層の表面側とAl合金基材側とで同一とするような従来形のポーラス層とバリア層を有する陽極酸化皮膜、或いは逆に、ポーラス層の表面側のポア径を、Al合金基材側に比して大きくするようなポーラス層とバリア層を有する陽極酸化皮膜では、前記熱応力差や応力を緩和することができない。また、表面側のポア径を、Al合金基材側に比して大きくすることは、耐プラズマ性などの基本特性を劣化させることにつながるため適切ではない。

【0030】このように、本発明では、前記熱応力差および応力の緩和のために、ポア径を表面側で小さく、か

つAl合金基材側で大きくしてなるように、陽極酸化皮膜を層構造または傾斜構造とする。より具体的には、通常の陽極酸化皮膜処理の範囲においては、Al合金基材側のポア径が5~100nmの範囲となるので、これに対応して、表面側のポア径を基材側のポア径の1/2~1/3以下と小さくすることが好ましい。なお、前記ポーラス層のポア径の変化は、深さ方向の任意区間で連続的な変化部を有していても、また、深さ方向の任意区間で非連続的な変化部を有していても構わない。

【0031】また、陽極酸化皮膜の前記バリア層の側を厚くすることによっても、前記応力を緩和し、陽極酸化皮膜の体積変化に伴う割れを防止する効果があり、更に、耐食性も向上させることができる。したがって、バリア層の厚みは30nm以上とすることが好ましい。このように陽極酸化皮膜のバリア層の厚さを制御すること、使用中に、陽極酸化皮膜とハロゲンなどの腐食性ガスやプラズマが接触した時に生じる応力や体積変化を緩和することができ、その結果、腐食や損傷の起点となる皮膜の割れや剥離を抑制して、Al合金表面と優れた密着性を発揮する。

【0032】ポーラス層とバリア層を含む陽極酸化皮膜全体の厚みは、陽極酸化皮膜の前記優れた耐食性を発揮させるためには、0.1μm以上が好ましく、1μm以上であればより好ましい。但し、陽極酸化皮膜の厚みが厚すぎると、内部応力の影響により割れを生じて、表面の被覆が不十分となったり、皮膜の剥離を引き起して、却って皮膜性能を阻害するので、皮膜の厚みは200μm以下、好ましくは100μm以下とすることが良い。

【0033】更に、本発明の好ましい他の態様として、陽極酸化皮膜中に、C、S、N、P、F、Bの内から選択された1種または2種以上の元素を含むことにより、陽極酸化皮膜自体の耐プラズマ性を向上させ、Al合金基材と陽極酸化皮膜との高温熱サイクルおよび高温腐食環境下での密着性を改善することができる。このためには、これら元素の内の最低1種が0.1%以上含有される必要がある。例えば、陽極酸化皮膜が前記元素の内のCの1種のみを0.1%以上含有すれば、他の元素含有量が0.1%未満の、0.01%程度の微量の含有の場合でも、Cとともに、その微量含有の元素が密着性向上効果を発揮する。

【0034】次いで、本発明における、陽極酸化乃至ペーマイト化あるいは擬ペーマイト化処理の方法について説明する。まず、陽極酸化皮膜を部分的にペーマイト化あるいは擬ペーマイト化する方法自体は、周知の水和処理などの方法が採用可能である。即ち、陽極酸化皮膜を設けたAl合金材料を、温水、加圧水、水蒸気等により、70~270℃の温度で、温水中に浸漬、または加圧水圧、水蒸気圧の雰囲気曝すことにより処理し、陽極酸化皮膜の表面をペーマイト化あるいは擬ペーマイト化する。しかし、このペーマイト化あるいは擬ペーマイト化は、前記特定の条件範囲にする必要があることは前記した通

りである。

【0035】次に、本発明における陽極酸化処理方法について説明する。まず、前記ポーラス層とボアの無いバリア層を有する陽極酸化皮膜を形成するとともに、更に、ポーラス層4の表面側のボア径を小さくする一方、ポーラス層4の基材側のボア径を大きくし、バリア層5を厚くした陽極酸化皮膜を形成する方法としては、前記特開平8-144088号や特開平8-260196号公報に開示された陽極酸化方法を用いることができる。

【0036】より具体的には、前記特開平8-144088号公報のように、陽極酸化の初期電圧を50V以下とするとともに陽極酸化の終期電圧を50V以上と高くして、前記ポーラス層とボアの無いバリア層を有する陽極酸化皮膜を形成しても良い。また、特開平8-260196号公報のように、まず、硫酸、りん酸、クロム酸などの溶液（電解液）で5～200Vの電解電圧により、ボアを有するポーラス層皮膜形成のためのポーラス型陽極酸化処理を施し、次いで、ほう酸系、りん酸系、フタル酸系、アジピン酸系、炭酸系、クエン酸系、酒石酸系などの溶液（電解液）で60～500Vの電解電圧により、ボアの無いバリア層皮膜形成のための非ポーラス型陽極酸化処理を施こしても良い。

【0037】更に、ポーラス層の表面側のボア径を基材側より小さくするためには、陽極酸化工程において、電解電圧を10～50V乃至10～80Vの範囲で変化させるとともに、ボア径を連続的に変化させる場合は、この電解電圧の変化を連続的に、ボア径を非連続的に変化させる場合は、この電解電圧の変化を断続的に変化させる。

【0038】また、前記した本発明の好ましい態様である、C、S、N、P、F、Bの元素の陽極酸化皮膜への含有は、しゅう酸、硫酸、ほう酸、りん酸、フタル酸、ぎ酸などの酸から選択される1種または2種以上の水溶液または混合水溶液を電解液とした陽極酸化により行う。この方法自体は、前記特開平8-193295号公報にも、具体的に開示されている。即ち、陽極酸化処理溶液として、例えばしゅう酸やぎ酸を用いると、 Al_4C_3 、 Al_2C_6 、 $HCOOH$ 、 $(COOH)_2$ 等のCを含む化合物が陽極酸化皮膜へ導入され、結果としてCが陽極酸化皮膜へ含有される。即ち、本発明ではC、S、N、P、F、Bの元素の陽極酸化皮膜への含有は、これら元素のイオン乃至化合物の形で行われて良い。

【0039】例えば、Sを陽極酸化皮膜へ含有する場合には、硫酸水溶液乃至硫酸や $Al_2(SO_4)_3$ 等を前記酸溶液に添加した水溶液での陽極酸化により、 H_2SO_4 、 H_2SO_3 、 $Al_2(SO_4)_3$ 、 $Al(HSO_4)_3$ などのSを含む化合物が陽極酸化皮膜へ導入される。また、Nを陽極酸化皮膜へ含有する場合には、 HNO_3 、 $Al(NO_3)_3$ 等を、前記酸溶液に添加することにより、 HNO_3 、 $Al(NO_3)_3$ などのNを含む化合物が陽極酸化皮膜へ導入され、結果としてNが陽極酸化皮膜へ含有される。更に、Pを陽極酸化皮膜へ含有す

る場合には、りん酸乃至りん酸塩水溶液での陽極酸化により、 H_3PO_4 、 H_3PO_3 、 $AlPO_4$ としてPが陽極酸化皮膜へ含有される。また、他の酸溶液に H_3PO_4 、 H_3PO_3 、 $AlPO_4$ を添加して陽極酸化しても良い。Fを陽極酸化皮膜へ含有する場合には、HFを前記酸溶液に添加することにより、Fが陽極酸化皮膜へ含有される。更に、Bを陽極酸化皮膜へ含有する場合には、 $(NH_3)_2B_4O_7$ や H_3BO_3 などを前記酸溶液に添加することにより、Bが $(NH_3)_2B_4O_7$ や B_2O_3 として陽極酸化皮膜へ含有される。

【0040】なお、これら元素を皮膜中に導入する陽極酸化処理条件は、C、S、N、P、F、Bの元素の内の最低1種が0.1%以上含有される条件によって決まるが、この際、C、S、N、P、F、Bの陽極酸化皮膜への導入量は、Al合金の組成や組織、および前記酸乃至これら酸の化合物の濃度、水溶液温度、攪拌条件、電流条件などの陽極酸化条件によっても異なるので、この条件を適宜調整して行う。陽極酸化の電解電圧を広い範囲で制御できる点からは、前記しゅう酸を1g/l以上含有する電解液が好ましい。そして、陽極酸化の電解電圧は、5～200Vの範囲から選択する。一方、本発明のAl材料は、半導体や液晶の製造装置などの真空容器用材料を主たる用途としているので、陽極酸化の電解液が半導体や液晶などの製品の汚染につながる元素を含むことは極力排除する。

【0041】更に、本発明に使用するAl合金について、特にMn:1.0～1.5%-Cu:0.05～0.20%などを含むJIS 3003A1合金、Mg:2.2～2.8%-Cr:0.15～0.35%などを含むJIS 5052Al合金、Cu:0.10～0.40%-Mg:0.5～1.5%-Cr:0.04～0.35%-Si:0.5～1.5%などを含むJIS 6061Al合金等が例示される。本発明におけるAl合金は、半導体や液晶の製造装置などの個々の真空容器の要求特性（強度、加工性、耐熱性など）に応じて、前記JIS 3003、5052、6061等やその他のJIS規格Al合金を適宜選択して使用することができる。勿論、これら既存の合金組成を変更したAl合金も使用可能である。

【0042】

【実施例】JIS 6061Al合金板に、陽極酸化処理を行い、表1に示す陽極酸化皮膜を設けた。陽極酸化処理は、後述するような酸を30～200g/l含有する電解液で、電解電圧を5～150Vにて陽極酸化を行い、ポーラス層とボアの無いバリア層を有する陽極酸化皮膜を設けた。この内、発明例No.1～7、比較例No.10、11は、ポーラス層の表面側のボア径を基材側より小さくするため、電解電圧を10～50V乃至10～80Vの範囲で変化させるとともに、ボア径を連続的に変化させる場合は、この電解電圧の変化を連続的に、ボア径を非連続的に変化させる場合は、この電解電圧の変化を断続的に変化させた。

【0043】この結果、2万倍の走査型電子顕微鏡で確認した陽極酸化皮膜構造は、ポーラス層とボアの無いバリア層を有する陽極酸化皮膜において、()図2のよう

にポーラス層のポア径を深さ方向に同じとした例(表1の比較例No.8、9)、() 図1のポア3aのようにポーラス層の表面側のポア径を基材側より小さくし、ポア径が任意区間で連続的变化部を有している例(表1の発明例No.2、5、6、比較例No.11)、() 図1のポア3bのようにポーラス層の表面側のポア径を基材側より小さくし、ポア径が任意区間で表1に記載した3段階の非連続的变化部を有している(ポア径の異なるポーラス層が3層構造となっている)例(表1の発明例No.1、3、4、7、比較例No.10)の3種類となっていた。陽極酸化皮膜のバリア層の厚みは、発明例と比較例ともに、全て50nm以上であった。

【0044】また、陽極酸化皮膜への各元素の含有は、Cの含有はしゅう酸、Pの含有はりん酸、Sの含有は硫酸あるいは亜硫酸を各々電解液として行った。そして、これらの元素を複合して含有させる場合は、元素の組み合わせに応じて、前記酸を各々混合した電解液により行った。より具体的には、例えば、Cの含有は電解液をしゅう酸(30g/l)、CとSとの含有は電解液をしゅう酸(30g/l)と硫酸(5g/l)との混酸、CとSとの含有は電解液をしゅう酸(30g/l)と硫酸(3g/l)との混酸、PとSとの含有は電解液をりん酸(60g/l)と硫酸(60g/l)との混酸とするなどして、酸の配合量を調節して各々の元素含有量を調整し、表1に示す各々の元素の所定量を陽極酸化皮膜へ含有させた。

【0045】そして、陽極酸化皮膜を設けたAl合金材料を、更に水蒸気により、180℃の温度で、2トールの水蒸気圧の雰囲気中に曝す水和処理を行い、ペーマイトあるいは擬ペーマイトが含有される陽極酸化皮膜の厚さを、皮膜厚さの5%以上、90%以下、また、陽極酸化皮膜の当該表面部分の、ペーマイトあるいは擬ペーマイトの含有量を、皮膜層に対する体積率で、20%以上、80%以下とすべく、ペーマイト化あるいは擬ペーマイト化した。これらのペーマイト化あるいは擬ペーマイト化の量も表1に示す。

【0046】なお、本実施例では、陽極酸化皮膜のペーマイト化あるいは擬ペーマイト化の量は、X線回折とX線光電子分光分析(XPS)の併用により、元の陽極酸化皮膜の組織である、Al-O、Al-OH、Al-O-OHとの識別および定量的な分析を行った。即ち、発明例と比較例の陽極酸化皮膜を厚み(深さ方向)に定量分析し、ペーマイトあるいは擬ペーマイトが含有される陽極酸化皮膜の皮膜表面からの厚さ(深さ、皮膜全体の膜厚に対する割合)、およびペーマイトあるいは擬ペーマイトの含有量(皮膜層に対する体積率)を、表1に定量的に示している。

【0047】そして、これらのペーマイト化あるいは擬ペーマイト化した陽極酸化皮膜を設けたAl合金板を、[Ⓢ]耐熱割れ性試験、[Ⓣ]耐ハロゲンガス腐食性試験、[Ⓤ]耐プラズマ腐食性試験、を各々行って、高温熱サイクルおよ

び腐食環境下での陽極酸化皮膜の割れ性およびガスおよびプラズマ耐食性を評価した。これらの結果も表1に示す。

【0048】なお、高温熱サイクルおよび高温腐食環境下での、ペーマイト化あるいは擬ペーマイト化した陽極酸化皮膜の[Ⓢ]耐熱割れ性試験の具体的な条件は、室温から250℃までの加熱を5サイクル行った後に、陽極酸化皮膜の表面状況を顕微鏡により観察し、皮膜の深さ方向への割れの発生状況を調査した。この結果、割れの発生が無いものを○、微小な割れが発生しているものを△、マクロ的な割れが発生しているものを×とした。

【0049】また、[Ⓣ]耐ハロゲンガス腐食性試験の具体的な条件は、半導体製造装置の実際の使用条件の内のより厳しい条件に合わせて、前記皮膜を設けたAl合金板の試験片を300℃の5%Cl₂含有Arガスに120分間暴露する試験を行い、暴露後の試験片の表面全面にテープを貼って剥がした際の、陽極酸化皮膜の剥離状況(剥離面積)を調査し、剥離がないものを○、剥離面積が試験片表面積の25%以下のものを△、剥離面積が試験片表面積の26%を越えて広がっているものを×として評価した。

【0050】更に、[Ⓤ]耐プラズマ腐食性試験の具体的な条件は、半導体製造装置での実際の使用条件の内のより厳しい条件に合わせて、前記皮膜を設けたAl合金板の試験片に、BCl₃プラズマ照射10分間および冷却5分間を6回繰り返した後の陽極酸化皮膜表面のエッチング量を顕微鏡により測定し、エッチング量が1ミクロン以下のものを○、エッチング量が1~3ミクロンのものを△、エッチング量が3ミクロンを越えるものを×として評価した。

【0051】表1から明らかな通り、陽極酸化皮膜が、(1)ポアを有するポーラス層とポアのないバリア層とを有し、かつ(2)前記ポーラス層のポア径を、陽極酸化皮膜の表面側で小さく、かつAl合金基材側で大きくしてなり、更に(3)ペーマイトあるいは擬ペーマイトが含有される皮膜表面からの厚さが5%以上、および(4)ペーマイトあるいは擬ペーマイトの含有量が20%以上からなる陽極酸化皮膜で、かつ(5)C、S、N、P、F、Bの元素をいずれか0.1%以上含有陽極酸化皮膜を形成した発明例No.1~7は、[Ⓢ]耐熱割れ性試験、[Ⓣ]耐ハロゲンガス腐食性試験、[Ⓤ]耐プラズマ腐食性試験、のいずれにおいても優れた結果が得られている。但し、発明例No.3、7は、ペーマイトあるいは擬ペーマイト化の量が比較的少なく、他の発明例に比して、ハロゲンガス腐食性が比較的劣っている。したがって、本発明の要件や好ましい要件を満足すれば、ガス耐食性やプラズマ耐食性に優れ、これを基本的に保証する陽極酸化皮膜の耐熱割れ性にも優れていることが分かる。

【0052】これに対し、表1から明らかな通り、比較例No.8、9は、本発明の他の要件は満足するものの、陽極酸化皮膜のポア径が表面側と基材側で同じであり、前

記(2)の要件を欠如し、ポア径を陽極酸化皮膜の表面側で小さくしておらず、陽極酸化皮膜が多層乃至傾斜構造を有していない単層構造である。また、比較例No.10、11は、各々前記(3)の要件を欠如し、ペーナイトあるいは擬ペーナイトが、前記陽極酸化皮膜厚さの5%未満しかなく、比較例No.11は、更に前記(4)の要件を欠如し、皮膜層の20%未満しか含有させていないものである。したがって、比較例No.8、9は、陽極酸化皮膜の耐熱割れ性および耐プラズマ腐食性が劣り、比較例No.10、11は、耐プラズマ腐食性と耐ハロゲンガス腐食性が、発明例よりも劣っている。また、比較例No.8、9はペーナイトあるいは擬ペーナイト化量が80%を越えていることも、耐熱割れ性や耐プラズマ腐食性を低下させる一因となっているものと考えられる。

【0053】この実施例から明らかな通り、本発明に係るAl材料は、高温熱サイクル下で、しかも、前記ガスやプラズマの腐食環境下にある、真空容器またはプロセス反応容器、あるいはこれら容器の内部で用いられる部材や材料用として優れており、中でも特に、CVDやPVDなどの化学的或いは物理的真空蒸着装置、またはドライエッチング装置などの半導体や液晶の製造装置等の、容器、あるいはこれら容器の内部で用いられる部材や材料用として優れていることが分かる。更に、本発明に係るAl材料は、これら以外の用途でも、建築材料や自動車材料などにも適用することができる。

【0054】

【表1】

略号	区分	陽 極 酸 化 皮 膜						①耐熱 割れ性 試験	②HCl 腐食 試験	③H ₂ O ₂ 腐食 試験
		ポ ア 径		皮膜含有元素 (wt%)	皮膜の 総膜厚 (μm)	ペーナイト/擬ペーナイト 化条件				
		ポア径(μm) 表面側/ 基材側	#7径の 変化			皮膜含 有物	厚さ×含有量 (%)			
1	発明例	20 / 40 ・ 80	非連続	C:1.0、S:0.3	50	①	20 × 80	○	○	○
2	発明例	35 / 95	連続	C:1.5	15	①+②	60 × 70	○	○	○
3	発明例	35 / 45 ・ 95	非連続	P:1.0、S:0.3	5	①+②	40 × 30	○	△	○
4	発明例	15 / 30 ・ 70	非連続	C:1.2、S:0.5	75	①	30 × 50	○	○	○
5	発明例	10 / 15 ・ 25	非連続	S:1.5	75	①+②	80 × 80	○	○	○
6	発明例	30 / 100	連続	C:1.5	10	①+②	60 × 60	○	○	○
7	発明例	20 / 45 ・ 60	非連続	C:1.2、S:0.5	45	②	20 × 25	○	△	○
8	比較例	25 / 25	無し	S:0.3	75	①	20 × 85	×	○	×
9	比較例	80 / 80	無し	C:1.5、S:0.3	50	①+②	60 × 95	×	○	×
10	比較例	35 / 45 ・ 95	非連続	P:1.0、S:0.3	5	①+②	20 × 3	○	×	△
11	比較例	10 / 25	連続	S:1.5	75	①	1 × 3	○	×	△

* 上記皮膜含有物において、①はペーナイト、②は擬ペーナイトで、①+②はこれらの混合物

【0055】

【発明の効果】以上説明した通り、本発明に係るAl材料によれば、高温熱サイクル下で、しかも、前記ガスやプラズマの腐食環境での、耐熱割れ性および耐食性に優れたAl材料を提供することができる。従って、本発明に係るAl材料の用途である、例えば半導体や液晶製造装置などの高効率化及び軽量化等を促進することができ、高性能の半導体や液晶製造の効率的な生産を可能にするなどの効果を奏するなど、工業的な価値の高い発明である。

【図面の簡単な説明】

【図1】本発明陽極酸化皮膜の概略構造を模式的に示す

説明図である。

【図2】従来の陽極酸化皮膜の概略構造を模式的に示す説明図である。

【符号の説明】

A、B:陽極酸化皮膜

1:Al合金基材

2:セル壁

3:ポア

4:ポーラス層

5:バリア層

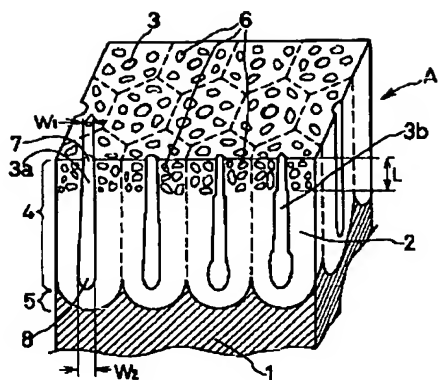
6:ペーナイト

～擬ペーナイト

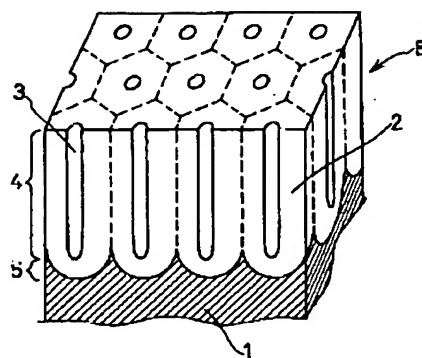
7:ポアの陽極酸化皮膜の表面側

8:ポアのAl合金基材側

【図1】



【図2】



フロントページの続き

(51)Int.Cl.⁶
H 0 1 L 21/3065

識別記号

F I
H 0 1 L 21/302

B

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-229185

(43)Date of publication of application : 24.08.1999

(51)Int.Cl.

C25D 11/04
C25D 11/18
// H01L 21/02
H01L 21/203
H01L 21/205
H01L 21/3065

(21)Application number : 10-031254

(71)Applicant : KOBE STEEL LTD

(22)Date of filing : 13.02.1998

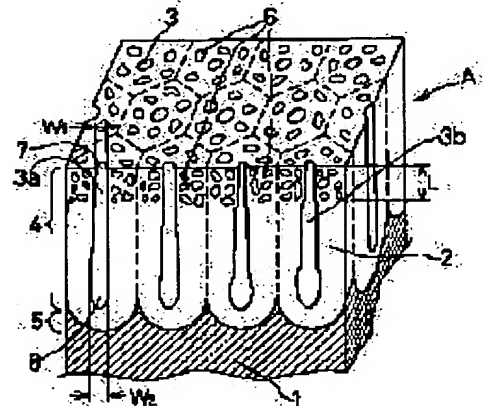
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(54) ALUMINUM MATERIAL EXCELLENT IN RESISTANCE TO HEAT CRACKING AND CORROSION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an Al material coated with an anodic oxide film excellent in resistance to the corrosion of gas and plasma without the anodic oxide film being cracked even in the corrosive environment of gas and plasma in a high- temp. heat cycle.

SOLUTION: An Al material with the anodic oxide film A having a porous layer 4 and a nonporous layer 5 formed on the surface is used as the Al material excellent in resistance to heat cracking and corrosion. In this case, the diameter of the pore 3 of the layer 4 on the surface side W1 is made smaller than that on the Al alloy substrate side W2, and boehmite and/or pseudoboehmite 6 are formed in the film.



LEGAL STATUS

[Date of request for examination]

21.09.2001

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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CLAIMS

[Claim(s)]

[Claim 1] It is aluminum ingredient with which the anodic oxide film which has the porous layer which has pore, and a barrier layer without pore was formed in the front face. As compared with aluminum alloy base material side, the front-face side of an anodic oxide film is made small for the diameter of pore of said porous layer. Further from an anodic oxide film front face in 5% or more of depth part of the thickness of film And the part more than 20 % is boehmite and/at the rate of the volume to a coat layer. Or aluminum ingredient excellent in the heat-resistant crack nature and corrosion resistance which are characterized by forming pseudo-boehmite.

[Claim 2] Said anodic oxide film front face to 90% of the thickness of film The part below 80 % is boehmite and/at the rate [as opposed to / are the following depth parts and / a coat layer] of the volume. Or aluminum ingredient excellent in the heat-resistant crack nature according to claim 1 and the corrosion resistance which form ** boehmite.

[Claim 3] Said anodic oxide film is C, S, N, P, F, and B. 1 chosen from inside A kind or 2 aluminum ingredient excellent in the heat-resistant crack nature according to claim 1 or 2 and the corrosion resistance which contain the element beyond a seed 0.1% or more.

[Claim 4] aluminum ingredient the diameter of pore of said porous layer excelled [ingredient] in heat-resistant crack nature given in claim 1 which has the discontinuous change section in the arbitration section of the depth direction thru/or any 1 term of 3, and corrosion resistance.

[Claim 5] aluminum ingredient the diameter of pore of said porous layer excelled [ingredient] in heat-resistant crack nature given in claim 1 which has the continuous change section in the arbitration section of the depth direction thru/or any 1 term of 4, and corrosion resistance.

[Claim 6] aluminum ingredient excellent in heat-resistant crack nature given in claim 1 said whose aluminum ingredient is a vacuum housing or an object for process reaction containers thru/or any 1 term of 5, and corrosion resistance.

[Claim 7] aluminum ingredient excellent in heat-resistant crack nature given in claim 1 said vacuum housing or whose process reaction container is an object for the manufacturing installations of a semi-conductor or liquid crystal thru/or any 1 term of 6, and corrosion resistance.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to aluminum ingredient suitable for vacuum housings, such as a semi-conductor and a manufacturing installation of liquid crystal, about aluminum ingredient in which the anodic oxide film was formed on aluminum alloy front face, as an ingredient which was especially excellent in the corrosion resistance of the heat-resistant crack nature under a high-temperature-corrosion environment and gas-proof, or the plasma-proof.

[0002]

[Description of the Prior Art] CVD PVD etc. -- the manufacturing installation of semi-conductors, such as a chemical or physical vacuum evaporation system or a dry etching system, or liquid crystal consists of primary members, such as a heater block, a chamber, a liner, a vacuum chuck, an electrostatic chuck, a clamper, bellows, bellows covering, a susceptor, a gaseous diffusion plate, and an electrode. the interior of the manufacturing installation of these semi-conductors or liquid crystal -- as reactant gas -- halogens, such as Cl, and F, Br, O and N, H, B, S, and C etc. -- corrosion resistance [as opposed to / since the corrosive gas containing an element is introduced / said corrosive gas in these primary members] (gas corrosion resistance) It is required. Moreover, since the plasma of a halogen system is also generated in addition to said corrosive gas, the corrosion resistance over this plasma is required of these primary members.

[0003] From the former, stainless steel has been used as this seed ingredient. However, with the demand of efficient-izing of a semi-conductor in recent years or the manufacturing installation of liquid crystal, or lightweight-izing, the member of thermal conductivity which used stainless steel is inadequate, and it has been a problem by it that weight is also large, and the whole equipment requires and weight-izes time amount at the time of equipment actuation etc. And heavy metal contained in stainless steel, such as nickel and Cr, is emitted into a process by a certain factor, and serves as a pollution source, and there is also a problem of degrading the quality of the product of a semi-conductor or liquid crystal.

[0004] For this reason, it replaces with this stainless steel, is lightweight, and is aluminum (henceforth aluminum) with high thermal conductivity. Use of an alloy is increasing rapidly. the inside of this aluminum alloy -- Mn:1.0-1.5%-Cu:0.05-0.20% etc. -- the included JIS 3003aluminum alloy and Mg:2.2-2.8%-Cr:0.15-0.35% etc. -- the JIS 6061aluminum alloy containing the included JIS 5052aluminum alloy, Cu:0.15-0.40%-Mg:0.8-1.2%-Cr:0.04-0.35%, etc. is used general-purpose. However, these aluminum alloy front face is not necessarily excellent in corrosion resistance to said corrosive gas or corrosive plasma. Therefore, in order to apply aluminum alloy as an ingredient for vacuum housings, such as a semi-conductor and a manufacturing installation of liquid crystal, it becomes indispensable conditions to improve the corrosion resistance over this gas and plasma. And in order to improve the corrosion resistance over gas and the plasma of aluminum alloy, it becomes the most effective means to perform a certain surface treatment to aluminum alloy front face.

[0005] Then, anodic oxidation which was excellent in corrosion resistance in order to raise the corrosion resistance over gas and plasma, such as a vacuum chamber member, (aluminum 2O₃) The technique which forms a coat in said aluminum alloy front face is Japanese Patent Publication No. 5-53870. It is proposed in the number. However, since the corrosion resistance over said gas and plasma changes greatly with membraneous qualities of a coat, this anodic oxide film cannot satisfy the demand of these corrosion resistance depending on the operating environment as a semiconductor-fabrication-machines-and-equipment member, either.

[0006] For this reason, various attempts which raise the membraneous quality of an anodic oxide film further are also proposed in order to improve the corrosion resistance of aluminum alloy as members, such as semiconductor fabrication machines and equipment. For example, in JP,8-144088,A, in case an anodic

oxide film is formed, making a telophase electrical potential difference higher than the initial voltage of anodic oxidation is proposed. Moreover, in JP,8-144089,A, anodizing is performed in the solution containing a sulfuric acid or phosphoric acid ion, and making the crevice on the front face of an anodic oxide film into the specific range is proposed. furthermore -- JP,8-260195,A and JP,8-260196,A -- first -- porous mold anodizing -- giving -- subsequently -- non-porous mold anodizing -- ***** -- things are proposed.

[0007] the conventional technique about these anodizing -- each -- drawing 2 as being shown -- base material aluminum alloy 1 a front face -- electrolysis initiation -- pore 3 Crevice called (hole) while forming -- aluminum alloy 1 Cel 2 which grows in the depth direction from -- becoming porous layer 4 Barrier layer 5 without pore from -- becoming anodic oxide film B It is based on preparing. It sets to such a usual anodic oxide film, and is drawing 2. It is pore 3 like. A path becomes the same at front-face [of an anodic oxide film], and aluminum alloy base material side. And barrier layer 5 which does not have pore in such anodic-oxidation-coatings structure Since it does not have gas permeability, gas and the plasma are the aluminum alloy 1. It has prevented contacting. Moreover, at JP,8-193295,A, it is this 2. In order to raise further the corrosion resistance over the plasma of the anodic oxide film of heavy structure, it is the porous layer 4. Making the diameter of pore and the diameter of a cel by the side of a front face as small as possible is proposed.

[0008]

[Problem(s) to be Solved by the Invention] It has the porous layer which has said a majority of pores, and a barrier layer without pore, and is the porous layer 4. Surely the anodic oxide film made small as the diameter of a cel of the diameter of pore by the side of a front face can be carried out is excellent in the corrosion resistance over said gas and plasma. however, the manufacture conditions of a semi-conductor or liquid crystal -- the latest efficient-izing and enlargement -- a very severe thing -- becoming -- **** -- gas, plasma condition nearby high concentration, and high density -- it has elevated-temperature-ized. therefore, the reaction container (chamber) a configuration member and the use member in the interior -- receiving -- halogens, such as Cl, and F, Br, O and N, H, B, S, and C etc. -- the corrosion resistance over corrosive gas and the corrosive plasma containing an element is required, and the demand is severer recent years still. On the other hand, in the anodic oxide film obtained by said anodizing, it cannot reply to the corrosion resistance demand to said this gas or plasma that are severe.

[0009] Moreover, heat-resistant demand to the charge of manufacturing installation material of the target semi-conductor [this invention] in one side (technical problem) It is severer recent years still. Especially, in the member for manufacturing installations of a semi-conductor, it is under the severe operating environment of receiving many heat cycles in a pyrosphere while in use according to the process conditions of manufacture of a semi-conductor as described above. For this reason, under this elevated-temperature heat cycle, a crack occurs in an anodic oxide film, a corrosion component trespasses upon the bottom of the corrosive environment of said gas and plasma from the crack of this anodic oxide film, and the anodic oxide film obtained by said anodizing has a problem of making aluminum alloy which is a base material corrode. Therefore, in order to fill the heat-resistant demand to the charge of manufacturing installation material of these semi-conductors, it is necessary to improve the heat-resistant crack nature which prevented crack generating of the anodic oxide film under an elevated-temperature heat cycle.

[0010] This invention is made paying attention to such a situation, under an elevated-temperature heat cycle, moreover, even if the purpose is under the corrosive environment of said gas and plasma, a crack does not occur in an anodic oxide film, but it tends to offer aluminum ingredients aluminum alloy which prepared the anodic oxide film which is moreover excellent with the corrosion resistance over said gas and plasma, i.e., for vacuum housings etc.

[0011]

[Means for Solving the Problem] In order to attain this purpose, the summary of this invention It is aluminum ingredient with which the anodic oxide film which has the porous layer which has pore, and a barrier layer without pore as an aluminum ingredient excellent in heat-resistant crack nature and corrosion resistance was formed in the front face. As compared with aluminum alloy base material side, the front-face side of an anodic oxide film is made small for the diameter of pore of said porous layer. Further from an anodic oxide film front face in 5% or more of depth part of the thickness of film And the part more than 20 % is boehmite and/at the rate of the volume to a coat layer. Or it is forming pseudo-boehmite.

[0012] It is the front face or the whole of anodic oxidation coatings Boehmite and/Or sealing with pseudo-boehmite itself is common knowledge. That is, aluminum alloy ingredient which prepared the anodic oxide film is processed with warm water, pressurization water, a steam, etc., and it is common knowledge about the front face or the whole of an anodic oxide film boehmite-ization or to form pseudo-boehmite, to seal the

pore of the porous layer of an anodic oxide film, and to raise the corrosion resistance of an anodic oxide film more.

[0013] However, the purpose of well-known sealing is conventionally [these] for raising more the corrosion resistance under general corrosive environment under the ambient atmosphere in which humidity thru/or salts, etc. of aluminum alloy ingredient which prepared the anodic oxide film exists, or atmospheric air. Therefore, it is not the corrosion resistance improvement purpose to the crack prevention of an anodic oxide film, gas, or the plasma of aluminum alloy ingredient which moreover prepared the anodic oxide film under the corrosive environment of said gas and plasma under an elevated-temperature heat cycle like this invention.

[0014] And aluminum alloy ingredient which prepared the anodic oxide film made into the object of sealing is not aimed at the thing of the structure of anodic oxide coating of the inclination structure to which the path of the pore of the porous layer of an anodic oxide film targetted [a diameter of pore of a porous layer like this invention] small the thing of the usual structure of anodic oxide coating which becomes the same for the front-face side of an anodic oxide film as compared with aluminum alloy base material side by front-face [of an anodic oxide film], and aluminum alloy base material side thru/or multilayer structure, either.

[0015] and -- a purpose [seal / the pore of a porous layer / well-known sealing / conventionally / these / completely] -- carrying out -- the anodic-oxidation-coatings coat whole -- boehmite-izing -- or pseudo-boehmite is formed. For this reason, boehmite-izing or the volume of an anodic oxide film formed into pseudo-boehmite changes a lot. (expansion) It carries out. Therefore, depending on the operating environment and conditions of aluminum ingredient, a crack occurs in the depth direction of an anodic oxide film, and the heat-resistant crack nature of an anodic oxide film and corrosion resistance deteriorate on the contrary. [like / said vacuum housing or for process reaction containers] Especially, moreover, the inclination does not bear use remarkably under the corrosive environment of said gas or plasma under said elevated-temperature heat cycle.

[0016] In order to prevent the crack accompanying said volume change of the anodic oxide film in such conventional sealing, even if it is under the corrosive environment of said gas and plasma, moreover, the thermal stress difference between the anodic oxide film produced in this environment and aluminum alloy base material and the stress generated inside an anodic oxide film are eased under said elevated-temperature heat cycle. (buffer) It is necessary to carry out. For this reason, in this invention, the front-face side of an anodic oxide film is made small for the diameter of pore of said porous layer as compared with aluminum alloy base material side. (it enlarging and making it become by aluminum alloy base material side small by the front-face side of an anodic oxide film) An anodic oxide film is made into multilayer structure or inclination structure. And let boehmite-izing of anodic oxidation coatings, or the amount of formation of pseudo-boehmite be the specific range from crack prevention of anodic oxidation coatings and a corrosion-resistant viewpoint.

[0017] Namely, preferably, under said elevated-temperature heat cycle, although it carries out to more than the initial complement for sealing pore in order to raise corrosion resistance even if boehmite-izing of anodic oxidation coatings or the amount of formation of pseudo-boehmite in this invention is under the corrosive environment of said gas and plasma, moreover It carries out to below an amount that the crack of an anodic oxide film produces with the thermal stress difference between the anodic oxide film produced in this environment, and aluminum alloy base material, and extent of the stress generated inside an anodic oxide film. Moreover, it is the fundamental views of this invention extent of the stress which generates the diameter of pore of said porous layer inside the thermal stress difference between the anodic oxide film which also produces extent which makes small the front-face side of an anodic oxide film as compared with aluminum alloy base material side in this environment, and aluminum alloy base material, and an anodic oxide film, and that these shall be eased and the effectiveness that the crack of an anodic oxide film can be prevented shall be attained substantially.

[0018] In addition, although sealing of the pore may be carried out as a result by formation of the boehmite of this invention, or pseudo-boehmite, at this invention, it is extent of the sealing. (perfect sealing and half-sealing) It is not a problem and the amount of the boehmite formed or pseudo-boehmite governs the heat-resistant crack nature and corrosion resistance which are made into the purpose to the last.

[0019]
 [Embodiment of the Invention] It is drawing 1 about the structure of anodic oxide coating of this invention based on this fundamental view. It is shown typically. this drawing 1 as being shown -- anodic oxide film A of this invention Base material aluminum alloy 1 a front face -- pore 3 having -- aluminum alloy 1 Cel 2 which grows in the depth direction from -- becoming porous layer 4 Barrier layer 5 without pore from -- it becomes. And pore 3 The diameter W1 of pore by the side of the front face of an anodic oxide film is made smaller than the diameter W2 of pore by the side of aluminum alloy base material, and it

does not matter even if change of this diameter of pore has the continuous change section like pore 3a in the arbitration section of the depth direction, and whether it has the discontinuous change section like pore 3b in the arbitration section of the depth direction or these are intermingled. In this invention, the case of pore 3a in which the diameter of pore has the continuous change section is called said inclination structure, and the case of pore 3b in which the diameter of pore has the discontinuous change section is called said multilayer structure. In addition, drawing 2 described above in the usual anodic oxide film It is pore 3 like. A path becomes the same at front-face [of an anodic oxide film], and aluminum alloy base material side.

[0020] and such anodic oxidation coatings A setting -- further -- bainite and/or pseudo-bainite 6 an anodic-oxidation-coatings front face to 5% or more of the thickness of film -- desirable -- 90% or less of coat depth (thickness) the rate [as opposed to a coat layer to the part of 1] of the volume -- 20% the above -- desirable -- 80% it contains below -- making -- the surface layer of anodic oxidation coatings -- partial -- boehmite-izing -- or pseudo-boehmite is made to form boehmite-izing or in this case, making pseudo-boehmite form -- mainly -- porous layer 4 of anodic oxidation coatings it is -- although -- it may result in a barrier layer depending on coat conditions

[0021] The boehmite or pseudo-boehmite said by this invention is the hydration oxide of aluminum, is expressed with general formula and $\text{Al}_2\text{O}_3 \cdot \text{XH}_2\text{O}$, and says the hydration oxide of aluminum generated by the hydration reaction of the oxide of aluminum of an anodic oxide film by hydration processing. And said X Generally the value is called boehmite or pseudo-boehmite in the thing of about 1-1.9.

[0022] Measurement of the amount of the boehmite in these anodic oxidation coatings or pseudo-boehmite is 2. It is difficult when the boehmite or pseudo-boehmite currently especially formed only by the gestalt-observation by the scanning electron microscope of 10,000 times or more is a detailed crystal. therefore, measurement of the amount of boehmite or pseudo-boehmite -- X Line diffraction and X Linear-light electron spectroscopy analysis (XPS) and infrared spectral-analysis method (FT-IR) etc. -- by using, it can measure correctly. For example, $\text{AlO} \leftrightarrow \text{H}$ which will be accepted in the 3000-3700 cm^{-1} neighborhood if the case of FT-IR is taken for an example The absorption spectrum by stretching vibration, And by accepting any one of the absorption spectrums by the stretching vibration of $\text{Aluminum} \leftrightarrow \text{OH}$ accepted in the 1050-1100 cm^{-1} neighborhood Existence of the hydration oxide film of aluminum is checked and they are the discernment from the amorphous tissue of the original anodic oxide film, and the depth of an anodic oxide film from the reinforcement of those spectrums. (thickness) Quantitative analysis of a direction is possible. Moreover, X In line diffraction, quantitative analysis is possible similarly from the X diffraction peak intensity of Aluminum-OOH .

[0023] Next, the quantitative conditions in this invention of boehmite-izing or the formation of pseudo-boehmite are explained. in order [first,] to raise the corrosion resistance under the corrosive environment of said gas and plasma in this invention -- the boehmite of anodic oxidation coatings, or the amount of pseudo-boehmite formation -- boehmite or pseudo-boehmite -- 5% or more of depth of an anodic-oxidation-coatings front face to the thickness of film -- desirable -- 40% the above depth -- and it is made to contain more than 50 % preferably more than 20 % at the rate of the volume to a coat layer

[0024] In addition, function of boehmite and pseudo-boehmite (effectiveness) It may be the same, and as for boehmite or pseudo-boehmite, it may be independent to make it form thru/or contain in anodic oxidation coatings, or it may be mixing.

[0025] If the thickness of the anodic oxide film which boehmite or pseudo-boehmite contains is less than 5% of the thickness of film, the corrosion resistance over gas or the plasma will become less enough. Moreover, the content of the boehmite or pseudo-boehmite of the surface part of anodic oxidation coatings concerned is 20% at the rate of the volume to a coat layer. The corrosion resistance over gas or the plasma becomes less enough also in the following.

[0026] On the other hand, with the stress which is produced in this invention under said elevated-temperature heat cycle and the corrosive environment of gas or the plasma and which is generated inside an anodic oxide film, and the thermal stress difference between aluminum alloy base materials and an anodic oxide film Thickness of the anodic oxidation coatings which boehmite or pseudo-boehmite contains in order to prevent that a crack arises in anodic oxidation coatings (depth) An upper limit 90% of the thickness of film It is 80% at the rate [as opposed to a coat layer for the upper limit of the content of the boehmite or pseudo-boehmite of the surface parts of the following and anodic oxidation coatings concerned] of the volume. Considering as the following is desirable.

[0027] It can prevent fundamentally that it is eased by multilayer-structure-izing and inclination structuring of an anodic oxide film which are one of the requirements for this invention and which make small the front-face side of an anodic oxide film for the diameter of pore as compared with aluminum alloy base

material side, and a crack produces said thermal stress difference and stress in an anodic oxide film by them. However, in order to prevent more certainly the crack of anodic oxidation coatings at the time of the operating environment of aluminum alloy ingredient becoming severer, the conditions of the desirable upper limit of boehmite-izing of said anodic oxidation coatings or the formation of pseudo-boehmite are needed. [0028] That is, the thickness of the anodic oxide film which boehmite or pseudo-boehmite contains is 90% of the thickness of film. If it exceeds Moreover, the content of the boehmite or pseudo-boehmite of the surface part of anodic oxidation coatings concerned is 80% at the rate of the volume to a coat layer. If it exceeds said conventional sealing -- the same -- anodic oxidation coatings -- substantial -- the coat whole -- said boehmite-izing -- or pseudo-boehmite is formed -- ***** -- change of the volume of anodic oxidation coatings (expansion) It becomes larger. For this reason, in case it becomes easy to generate a crack in the depth direction of an anodic oxide film and the operating environment of said aluminum alloy ingredient becomes severer in it, it is because the crack nature of an anodic oxide film and corrosion resistance may result in deteriorating on the contrary.

[0029] Next, in order to prevent the crack accompanying the volume change of an anodic oxide film in the anodic oxide film which has a porous layer and a barrier layer as describe above, the anodic oxide film itself eases the stress moreover generate also under the corrosive environment of said gas and plasma inside the thermal stress difference between the anodic oxide film produce in this environment, and aluminum alloy base material, and an anodic oxide film under said elevated temperature heat cycle. (buffer) It is needed that it is the make structure. As an improvement of the structure of anodic oxide coating for this itself, it has chosen making small the diameter of pore by the side of the front face of a porous layer as compared with aluminum alloy base material side by this invention. Said thermal stress difference or stress cannot be eased in the anodic oxide film which has a formal porous layer and a formal barrier layer as other modes conventionally which makes the diameter of pore the same at front-face [of a porous layer], and aluminum alloy base material side, or the anodic oxide film which has conversely a porous layer which enlarges the diameter of pore by the side of the front face of a porous layer as compared with aluminum alloy base material side, and a barrier layer. Moreover, since it is connected with degrading basic properties, such as plasma-proof nature, it is not appropriate to enlarge the diameter of pore by the side of a front face as compared with aluminum alloy base material side.

[0030] Thus, in this invention, an anodic oxide film is made into layer structure or inclination structure so that the diameter of pore may be small enlarged by aluminum alloy base material side by the front-face side and it may become for relaxation of said thermal stress difference and stress. More specifically in the range of the usual anodic oxide film processing, the diameter of pore by the side of aluminum alloy base material Since it becomes the range of 5 - 100 nm, it corresponds to this, and it is a diameter of pore by the side of a front face 1/2 - 1/3 of the diameter of pore by the side of a base material It is desirable to make it small the following. In addition, whether it has the continuous change section in the arbitration section of the depth direction or change of the diameter of pore of said porous layer has the discontinuous change section in the arbitration section of the depth direction, it is not cared about.

[0031] Moreover, also by thickening said barrier layer side of anodic oxidation coatings, said stress is eased, it is effective in preventing the crack accompanying the volume change of anodic oxidation coatings, and corrosion resistance can also be raised further. Therefore, it is desirable to set thickness of a barrier layer to 30nm or more. Thus, the crack of a coat and exfoliation which can ease the stress and the volume change which are produced when corrosive gas and plasma, such as anodic oxidation coatings and a halogen, contact, consequently serve as an origin of corrosion or damage during use are controlled, and controlling the thickness of the barrier layer of anodic oxidation coatings also demonstrates aluminum alloy front face and the outstanding adhesion.

[0032] The thickness of the whole anodic oxide film containing a porous layer and a barrier layer is 0.1 in order to demonstrate said outstanding corrosion resistance of an anodic oxide film. mum The above is desirable and it is 1. mum It is more desirable if it is above. However, if the thickness of an anodic oxide film is too thick, since a crack is produced under the effect of internal stress, surface covering will become inadequate, or exfoliation of a coat will be caused and the coat engine performance will be checked on the contrary, the thickness of a coat is 200. mum It is 100 preferably hereafter. mum It is good to consider as the following.

[0033] Furthermore, they are C, S, N, P, F, and B in an anodic oxide film as other modes with desirable this invention. 1 chosen from inside A kind or 2 By including the element beyond a seed, the plasma-proof nature of the anodic oxide film itself can be raised, and the elevated-temperature heat cycle of aluminum alloy base material and an anodic oxide film and the adhesion under a high-temperature-corrosion environment can be improved. For that, it is at least 1 of these elements. A seed needs to contain 0.1% or

more. For example, an anodic oxide film is C of said elements. 1 If only a seed is contained 0.1% or more, other element contents will be 0.01 less than 0.1%. It is C even when it is content of the minute amount which is extent. The element of the minute amount content demonstrates the improvement effectiveness in adhesion.

[0034] Subsequently, the approach of the anodization thru/or boehmite-izing in this invention, or pseudo-boehmite-ized processing is explained. First, boehmite-izing or the approach itself formed into pseudo-boehmite can adopt approaches, such as well-known hydration processing, for anodic oxidation coatings partially. namely, the thing which aluminum alloy ingredient which prepared the anodic oxide film is put to the ambient atmosphere of immersion or pressurization water pressure, and a water vapor pressure into warm water at the temperature of 70 - 270 °C with warm water, pressurization water, a steam, etc. -- processing -- the front face of an anodic oxide film -- boehmite-izing -- or pseudo-boehmite is formed. However, it is as having described above that it is necessary to make this boehmite-izing or pseudo-boehmite-ization into said specific condition range.

[0035] Next, the anodizing approach in this invention is explained. First, while forming the anodic oxide film which has said porous layer and a barrier layer without pore, it is the porous layer 4 further. While making small the diameter of pore by the side of a front face, it is the porous layer 4. The diameter of pore by the side of a base material is enlarged, and it is the barrier layer 5. As an approach of forming the thickened anodic oxide film, the anodic oxidation approach indicated by said JP,8-144088,A and JP,8-260196,A can be used.

[0036] More specifically, it is 50V about the initial voltage of anodic oxidation like said JP,8-144088,A. While considering as the following, it is 50V about the telophase electrical potential difference of anodic oxidation. It may be made high with the above and the anodic oxide film which has said porous layer and a barrier layer without pore may be formed. Moreover, they are solutions, such as a sulfuric acid, phosphoric acid, and a chromic acid, first like JP,8-260196,A. (electrolytic solution) With the electrolytic voltage of 5 - 200V Porous mold anodizing for the porous layer coat formation which has pore is performed. Subsequently Solutions, such as a way acid system, a phosphoric acid system, a phthalic-acid system, an adipic-acid system, a carbonic acid system, a citric-acid system, and a tartaric-acid system (electrolytic solution) ***** is also good in non-porous mold anodizing for the barrier layer coat formation which does not have pore by the electrolytic voltage of 60-500V.

[0037] Furthermore, in order to make the diameter of pore by the side of the front face of a porous layer smaller than a base material side, it sets at an anodic oxidation process, and it is 10-50V about electrolytic voltage. Or 10-80V When changing the diameter of pore continuously, and change of this electrolytic voltage changes the diameter of pore in discontinuous continuously, change of this electrolytic voltage is changed [while making it change in the range,] intermittently.

[0038] Moreover, C which is the desirable mode of above mentioned this invention, S, N, P, F, and B The content to the anodic oxide film of an element is 1 chosen from acids, such as oxalic acid, a sulfuric acid, a way acid, phosphoric acid, a phthalic acid, and formic acid. A kind or 2 The anodic oxidation which used the water solution or mixed water solution beyond a seed as the electrolytic solution performs. This approach itself is concretely indicated by said JP,8-193295,A. namely, -- if for example, an oxalic acid goat acid is used as an anodizing solution -- aluminum₄C₃, aluminum₂C₅, HCOOH, and 2 (COOH) etc. -- C the included compound introduces to an anodic oxide film -- having -- as a result -- C It contains to an anodic oxide film. That is, at this invention, they are C, S, N, P, F, and B. Content to the anodic oxide film of an element may be performed in the ion of these elements thru/or the form of a compound.

[0039] for example, S the case where it contains to an anodic oxide film -- a sulfuric-acid water solution thru/or a sulfuric acid, and aluminum₂(SO₄)₃ etc. -- anodic oxidation, with the water solution added in said acid solution -- H₂SO₄, H₂SO₃, aluminum₂(SO₄)₃, and aluminum (HSO₄)₃ etc. -- S The included compound is introduced to an anodic oxide film. Moreover, N They are N, such as HNO₃ and aluminum (NO₃)₃, by adding HNO₃ and aluminum(NO₃)₃ grade in said acid solution, in containing to an anodic oxide film. The included compound is introduced to an anodic oxide film, and it is N as a result. It contains to an anodic oxide film. furthermore, P the case where it contains to an anodic oxide film -- anodic oxidation, with phosphoric acid thru/or a phosphoric acid salt water solution -- H₃PO₄ and H₃ -- PHO₃ and AlPO₄ ***** -- P It contains to an anodic oxide film. Moreover, they are H₃PO₄, H₃PO₃, and AlPO₄ to other acid solutions. You may add and anodize. F It is F by adding HF in said acid solution, in containing to *****. It contains to an anodic oxide film. furthermore, B the case where it contains to an anodic oxide film -- 2B (NH₃)₄O₇ and H₃BO₃ etc. -- adding in said acid solution -- B It contains to an anodic oxide film as 2B (NH₃)₄O₇ or B-2 O₃.

[0040] In addition, the anodizing conditions which introduce these elements into a coat are C, S, N, P, F,

and B. At least 1 of the elements Although a seed is decided by the conditions contained 0.1% or more Under the present circumstances, C, S, N, P, F, and B Since the amount of installation to an anodic oxide film changes also with anodic oxidation conditions, such as concentration of the compound of a presentation and organization of aluminum alloy and said acid thru/or these acids, water-solution temperature, stirring conditions, and current conditions, this condition is adjusted suitably and it performs it. The electrolytic solution which contains 1 or more g/l of said oxalic acid from the point which can control the electrolytic voltage of anodic oxidation in the large range is desirable. And the electrolytic voltage of anodic oxidation is chosen from the range of 5 -200V. On the other hand, since aluminum ingredient of this invention makes the main application charges of vacuum housing material, such as a semi-conductor and a manufacturing installation of liquid crystal, it eliminates it that the element with which the electrolytic solution of anodic oxidation leads to contamination of products, such as a semi-conductor and liquid crystal, is included as much as possible.

[0041] furthermore, the JIS 3003aluminum alloy which contains Mn:1.0-1.5%-Cu:0.05-0.20% etc. especially about aluminum alloy used for this invention, and Mg:2.2-2.8%-Cr:0.15-0.35% etc. -- the JIS 6061aluminum alloy containing the included JIS 5052aluminum alloy, Cu:0.10 -0.40%-Mg:0.5-1.5%-Cr:0.04-0.35%-Si:0.5-1.5%, etc. is illustrated. aluminum alloys in this invention are the demand characteristics of each vacuum housings, such as a semi-conductor and a manufacturing installation of liquid crystal. s (reinforcement, workability, thermal resistance, etc.) It responds and is JIS of said JIS 3003, 5052, 6061 grades, or others. A specification aluminum alloy can be used choosing it suitably. Of course, aluminum alloy which changed the alloy presentation of these existing is also usable.

[0042]

[Example] Anodizing is performed to a JIS 6061aluminum alloy plate, and it is Table 1. The shown anodic oxide film was prepared. Anodizing was the electrolytic solution which carries out 30-200 g/l content of the acid which is mentioned later, anodized electrolytic voltage in 5 -150V, and prepared the anodic oxide film which has a porous layer and a barrier layer without pore. Among this, example No.of invention1-7, example No.of comparison 10, and 11 In order to make the diameter of pore by the side of the front face of a porous layer smaller than a base material side, it is 10-50V about electrolytic voltage. Or 10-80V While making it change in the range, when changing the diameter of pore continuously When change of this electrolytic voltage changed the diameter of pore in discontinuous continuously, change of this electrolytic voltage was changed intermittently.

[0043] Consequently, 2 The structure of anodic oxide coating checked with the 10,000 times as many scanning electron microscope as this the anodic oxide film which has a porous layer and a barrier layer without pore -- setting -- (**) Drawing 2 Example which made the diameter of pore of a porous layer the same as the depth direction like (8 example Noof comparison. of Table 1 9) (b) The diameter of pore by the side of the front face of a porous layer is made smaller than a base material side like pore 3a of drawing 1. example for which the diameter of pore has the continuous change section in the arbitration section (example Noof invention. of Table 1 -- 2 and 5 --) 6 Example No.of comparison 11 (Ha) Drawing 1 The diameter of pore by the side of the front face of a porous layer is made smaller than a base material side like like pore 3b. The diameter of pore is Table 1 in the arbitration section. 3 indicated It has the gradual discontinuous change section. (the porous layer from which the diameter of pore differs is 3 it has layer structure) Example (example Noof invention. of Table 1 1, 3, 4, 7, example Noof comparison. 10) 3 It had become a class. The example of invention and the example of a comparison of the thickness of the barrier layer of anodic oxidation coatings were 50nm or more altogether.

[0044] Moreover, content of each element to an anodic oxide film is C. Content is oxalic acid and P. Content is phosphoric acid and S. Content performed the sulfuric acid or the sulfurous acid as the electrolytic solution respectively. And when making these elements compound and contain, according to the combination of an element, the electrolytic solution mixed respectively performed said acid. It is more specifically C. Content the electrolytic solution Oxalic acid (30 g/l), C S Content is oxalic acid (30 g/l) about the electrolytic solution. A mixed acid with a sulfuric acid (5 g/l), C S Content is oxalic acid (30 g/l) about the electrolytic solution. A mixed acid with a sulfuric acid (3 g/l), and P and S Content is phosphoric acid (60 g/l) about the electrolytic solution. Sulfuric acid (60 g/l) It considers as a mixed acid. The loadings of an acid are adjusted, each element content is adjusted, and it is Table 1. The specified quantity of each shown element was made to contain to an anodic oxide film.

[0045] Further aluminum alloy ingredient which prepared the anodic oxide film with a steam and at the temperature of 180 ** 2 The thickness of the anodic oxide film which performs hydration processing put to the ambient atmosphere of the water vapor pressure of a toll, and boehmite or pseudo-boehmite contains 5% or more of the thickness of film, and 90% the rate [as opposed to a coat layer for the content of the

boehmite or pseudo-boehmite of the surface parts of the following and anodic oxidation coatings concerned] of the volume -- 20% the above -- 80% the following -- it should carry out -- boehmite-izing -- or pseudo-boehmite was formed. The amount of these boehmite-izing or the formation of pseudo-boehmite is also Table 1. It is shown.

[0046] In addition, at this example, the amount of boehmite-izing of anodic oxidation coatings or the formation of pseudo-boehmite is X. Line diffraction and X Linear-light electron spectroscopy analysis (XPS) Concomitant use performed discernment and quantitative analysis with aluminum-O which is the tissue of the original anodic oxidation coatings, aluminum-OH, and aluminum-O-OH. That is, it is thickness about the anodic oxidation coatings of the example of invention, and the example of a comparison. (the depth direction) Thickness from the coat front face of the anodic oxidation coatings which carry out quantitative analysis and which boehmite or pseudo-boehmite contains (rate % to the thickness of the depth and the whole coat) And content of boehmite or pseudo-boehmite (rate of volume % to a coat layer) Table 1 It is shown quantitatively.

[0047] And the line evaluated [aluminum alloy plate which prepared these boehmite-izing or anodic oxide films which were formed into pseudo-boehmite] the crack nature of the anodic oxide film under an elevated-temperature heat cycle and corrosive environment, gas, and plasma corrosion resistance for ** heatproof crack sex test, the halogen-proof [**] gas corrosive trial, and the plasma-proof [**] corrosive trial respectively. These results are also Table 1. It is shown.

[0048] In addition, the concrete conditions of ** heatproof crack sex test of the boehmite-izing or the anodic oxide film formed into pseudo-boehmite under an elevated-temperature heat cycle and a high-temperature-corrosion environment are heating from a room temperature to 250 ** 5 After cycle *****, the surface situation of an anodic oxide film was observed under the microscope, and the generating situation of the crack to the depth direction of a coat was investigated. Consequently, that in which ** and a macro-crack have generated that in which O and a minute crack have generated the thing without generating of a crack was made into x.

[0049] Moreover, the concrete conditions of a halogen-proof [**] gas corrosive trial It doubles with the severer conditions of the actual service conditions of semiconductor fabrication machines and equipment. 300 ** is Cl₂ 5% about the test piece of aluminum alloy plate which prepared said coat. It is 120 to content Ar gas. The trial exposed between parts is performed. Exfoliation situation of an anodic oxide film at the time of sticking and removing a tape all over the front face of the test piece after exposure (stripped plane product) It investigates. O and a stripped plane product are 25% of test piece surface area about a thing without exfoliation. ** and a stripped plane product are as follows 26% of test piece surface area. What has exceeded and spread was evaluated as x.

[0050] Furthermore, the concrete conditions of a plasma-proof [**] corrosive trial It doubles with the severer conditions of the actual service conditions in semiconductor fabrication machines and equipment. To the test piece of aluminum alloy plate which prepared said coat, it is the cooling 5 for [BCl₃ plasma exposure] 10 minutes. It is between parts 6 The amount of etching on the front face of anodic oxidation coatings after ***** is measured under a microscope. The amount of etching is 1. O and the amount of etching are as follows [a micron] 1-3. ** and the amount of etching are the thing of a micron 3 The thing exceeding a micron was evaluated as x.

[0051] Table 1 since -- a clear passage -- anodic oxidation coatings -- (1) It has the porous layer which has pore, and a barrier layer without pore. And (2) In the diameter of pore of said porous layer, are small at the front-face side of an anodic oxide film. And it comes to enlarge by aluminum alloy base material side, and is (3) further. The thickness from the coat front face which boehmite or pseudo-boehmite contains 5% or more, And (4) The content of boehmite or pseudo-boehmite is 20%. With the anodic oxide film which consists of the above (5) -- C, S, N, P, F, and B Example No. of invention 1-7 which formed the content anodic oxide film for the element any 0.1% or more The result of having excelled also in ** heatproof crack sex test, a halogen-proof [**] gas corrosive trial, a plasma-proof [**] corrosive trial, and ***** is obtained. [and] however, example No. of invention. -- 3 and 7 There are comparatively few amounts of boehmite or the formation of pseudo-boehmite, and a halogen gas corrosive is comparatively inferior as compared with other examples of invention. Therefore, if the requirements and the desirable requirements for this invention are satisfied, it turns out that it excels in gas corrosion resistance or plasma corrosion resistance, and excels also in the heat-resistant crack nature of an anodic oxide film which guarantees this fundamentally.

[0052] on the other hand, table 1 from -- a clear passage -- example No. of comparison. -- 8 and 9 although other requirements for this invention are satisfied -- the diameter of pore of an anodic oxide film -- a front-face side and a base material side -- the same -- the above (2) It is lacking in requirements, and the diameter of pore is not made small by the front-face side of an anodic oxide film, but an anodic oxide film is the

monolayer structure where it does not have a multilayer thru/or inclination structure. moreover, example Noof comparison. -- 10 and 11 -- the each above (3) requirements -- lacking -- boehmite or pseudo-boehmite -- said less than 5% of anodic oxide film thickness -- there is nothing -- example No.of comparison 11 further -- the above (4) It is lacking and under 20 % of a coat layer is not making requirements contain. therefore, example Noof comparison. -- 8 and 9 The heat-resistant crack nature of an anodic oxide film and a plasma-proof corrosive are inferior, and example No.of comparison 10 and 11 are inferior to the example of invention in a plasma-proof corrosive and a halogen-proof gas corrosive. moreover, example Noof comparison. -- 8 and 9 It is also thought that that the amount of formation of boehmite or pseudo-boehmite is over 80% is the cause to which it reduces heat-resistant crack nature and a plasma-proof corrosive. [0053] aluminum ingredient concerning this invention a passage clear from this example Moreover under an elevated-temperature heat cycle, it is under the corrosive environment of said gas and plasma. It excels as the member used inside a vacuum housing, a process reaction container, or these containers, or an object for ingredients. inside -- especially -- CVD PVD etc. -- it turns out chemical or that it excels as the member used inside containers, such as a manufacturing installation of semi-conductors, such as a physical vacuum evaporation system or a dry etching system, or liquid crystal, or these containers, or an object for ingredients. Furthermore, aluminum ingredient concerning this invention is applicable to a building material, an automobile ingredient, etc. also for applications other than these.

[0054]

[Table 1]

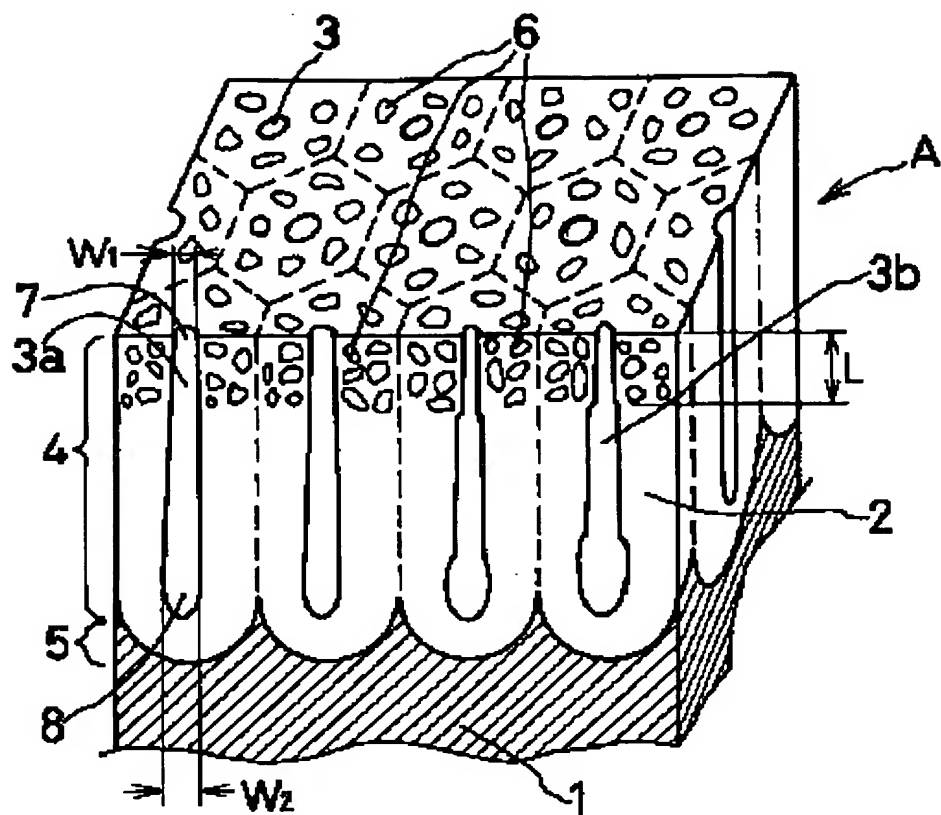
略号	区分	隔 極 酸 化 皮 膜						①耐熱 割れ性 試験	②H ₂ O ₂ 腐食 試験	③F ₂ /F ₂ O ₂ 腐食 試験
		ポア径		皮膜含有元素 (wt%)	皮膜の 総膜厚 (μm)	ペーナイト/擬ペーナイト 化条件				
		ポア径(mm) 表面側・基材側	孔径の 変化			皮膜含 有物	厚さ×含有量 (%)			
1	発明例	20 / 40・80	非連続	C:1.0、S:0.3	50	①	20×80	○	○	○
2	発明例	35・ / 95	連続	C:1.5	15	①+②	60×70	○	○	○
3	発明例	35 / 45・95	非連続	P:1.0、S:0.3	5	①+②	40×30	○	△	○
4	発明例	15 / 30・70	非連続	C:1.2、S:0.5	75	①	30×50	○	○	○
5	発明例	10 / 15・25	非連続	S:1.5	75	①+②	80×80	○	○	○
6	発明例	30・100	連続	C:1.5	10	①+②	60×60	○	○	○
7	発明例	20 / 45 60	非連続	C:1.2、S:0.5	45	②	20×25	○	△	○
8	比較例	25・25	無し	S:0.3	75	①	20×85	×	○	×
9	比較例	80 / 80	無し	C:1.5、S:0.3	50	①+②	60×95	×	○	×
10	比較例	35 / 45・95	非連続	P:1.0、S:0.3	5	①+②	20×3	○	×	△
11	比較例	10 / 25	連続	S:1.5	75	①	1×3	○	×	△

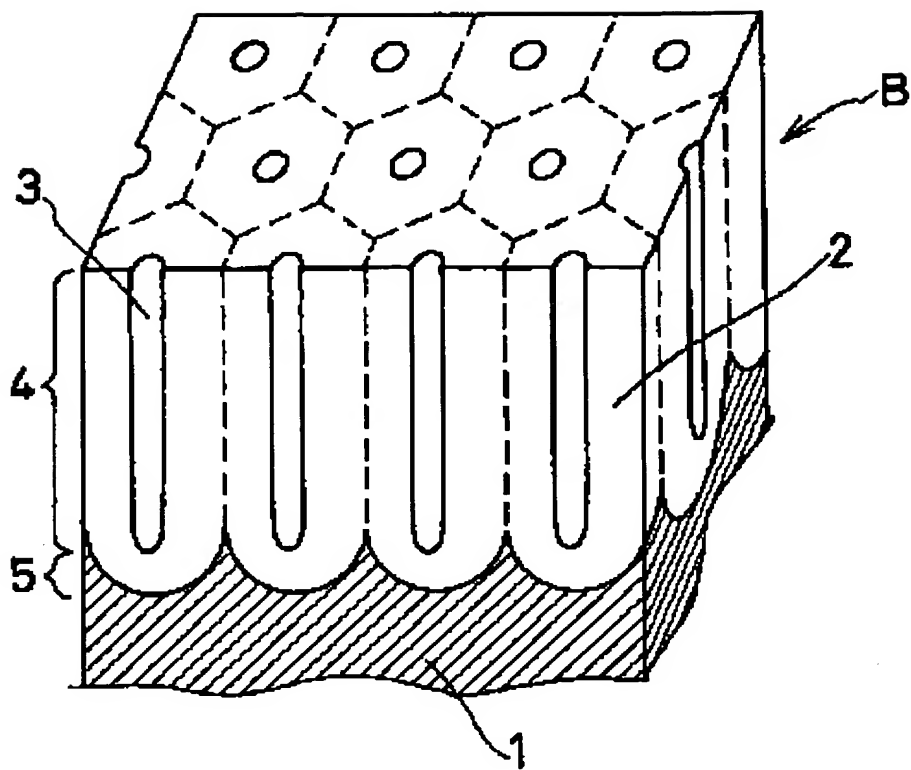
* 上記皮膜含有物において、①はペーナイト、②は擬ペーナイトで、①+②はこれらの混合物

[0055]

[Effect of the Invention] According to the aluminum ingredient concerning this invention, moreover, aluminum ingredient excellent in the heat-resistant crack nature and corrosion resistance in the corrosive environment of said gas and plasma can be offered under an elevated-temperature heat cycle as explained above. Therefore, it is invention with industrial high value, such as being able to promote efficient-izing, lightweight-izing, etc. of a semi-conductor, a liquid crystal manufacturing installation, etc., and doing so effectiveness, such as enabling efficient production of the semi-conductor of high performance, or liquid crystal manufacture, which is the application of aluminum ingredient concerning this invention.

[Translation done.]





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TECHNICAL FIELD

[Industrial Application] This invention relates to aluminum ingredient suitable for vacuum housings, such as a semi-conductor and a manufacturing installation of liquid crystal, about aluminum ingredient in which the anodic oxide film was formed on aluminum alloy front face, as an ingredient which was especially excellent in the corrosion resistance of the heat-resistant crack nature under a high-temperature-corrosion environment and gas-proof, or the plasma-proof.

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PRIOR ART

[Description of the Prior Art] CVD PVD etc. -- the manufacturing installation of semi-conductors, such as a chemical or physical vacuum evaporation system or a dry etching system, or liquid crystal consists of primary members, such as a heater block, a chamber, a liner, a vacuum chuck, an electrostatic chuck, a clamper, bellows, bellows covering, a susceptor, a gaseous diffusion plate, and an electrode. the interior of the manufacturing installation of these semi-conductors or liquid crystal -- as reactant gas -- halogens, such as Cl, and F, Br, O and N, H, B, S, and C etc. -- corrosion resistance [as opposed to / since the corrosive gas containing an element is introduced / said corrosive gas in these primary members] (gas corrosion resistance) It is required. Moreover, since the plasma of a halogen system is also generated in addition to said corrosive gas, the corrosion resistance over this plasma is required of these primary members.

[0003] From the former, stainless steel has been used as this seed ingredient. However, with the demand of efficient-izing of a semi-conductor in recent years or the manufacturing installation of liquid crystal, or lightweight-izing, the member of thermal conductivity which used stainless steel is inadequate, and it has been a problem by it that weight is also large, and the whole equipment requires and weight-izes time amount at the time of equipment actuation etc. And heavy metal contained in stainless steel, such as nickel and Cr, is emitted into a process by a certain factor, and serves as a pollution source, and there is also a problem of degrading the quality of the product of a semi-conductor or liquid crystal.

[0004] For this reason, it replaces with this stainless steel, is lightweight, and is aluminum (henceforth aluminum) with high thermal conductivity. Use of an alloy is increasing rapidly. the inside of this aluminum alloy -- Mn:1.0-1.5%-Cu:0.05-0.20% etc. -- the included JIS 3003aluminum alloy and Mg:2.2-2.8%-Cr:0.15-0.35% etc. -- the JIS 6061aluminum alloy containing the included JIS 5052aluminum alloy, Cu:0.15-0.40%-Mg:0.8-1.2%-Cr:0.04-0.35%, etc. is used general-purpose. However, these aluminum alloy front face is not necessarily excellent in corrosion resistance to said corrosive gas or corrosive plasma. Therefore, in order to apply aluminum alloy as an ingredient for vacuum housings, such as a semi-conductor and a manufacturing installation of liquid crystal, it becomes indispensable conditions to improve the corrosion resistance over this gas and plasma. And in order to improve the corrosion resistance over gas and the plasma of aluminum alloy, it becomes the most effective means to perform a certain surface treatment to aluminum alloy front face.

[0005] Then, anodic oxidation which was excellent in corrosion resistance in order to raise the corrosion resistance over gas and plasma, such as a vacuum chamber member, (aluminum 2O3) The technique which forms a coat in said aluminum alloy front face is Japanese Patent Publication No. 5-53870. It is proposed in the number. However, since the corrosion resistance over said gas and plasma changes greatly with membraneous qualities of a coat, this anodic oxide film cannot satisfy the demand of these corrosion resistance depending on the operating environment as a semiconductor-fabrication-machines-and-equipment member, either.

[0006] For this reason, various attempts which raise the membraneous quality of an anodic oxide film further are also proposed in order to improve the corrosion resistance of aluminum alloy as members, such as semiconductor fabrication machines and equipment. For example, in JP,8-144088,A, in case an anodic oxide film is formed, making a telophase electrical potential difference higher than the initial voltage of anodic oxidation is proposed. Moreover, in JP,8-144089,A, anodizing is performed in the solution containing a sulfuric acid or phosphoric acid ion, and making the crevice on the front face of an anodic oxide film into the specific range is proposed. furthermore -- JP,8-260195,A and JP,8-260196,A -- first -- porous mold anodizing -- giving -- subsequently -- non-porous mold anodizing -- ***** -- things are proposed.

[0007] the conventional technique about these anodizing -- each -- drawing 2 as being shown -- base material aluminum alloy 1 a front face -- electrolysis initiation -- pore 3 Crevice called (hole) while forming

-- aluminum alloy 1 Cel 2 which grows in the depth direction from -- becoming porous layer 4 Barrier layer 5 without pore from -- becoming anodic oxide film B It is based on preparing. It sets to such a usual anodic oxide film, and is drawing 2. It is pore 3 like. A path becomes the same at front-face [of an anodic oxide film], and aluminum alloy base material side. And barrier layer 5 which does not have pore in such anodic-oxidation-coatings structure Since it does not have gas permeability, gas and the plasma are the aluminum alloy 1. It has prevented contacting. Moreover, at JP,8-193295,A, it is this 2. In order to raise further the corrosion resistance over the plasma of the anodic oxide film of heavy structure, it is the porous layer 4. Making the diameter of pore and the diameter of a cel by the side of a front face as small as possible is proposed.

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EFFECT OF THE INVENTION

[Effect of the Invention] According to the aluminum ingredient concerning this invention, moreover, aluminum ingredient excellent in the heat-resistant crack nature and corrosion resistance in the corrosive environment of said gas and plasma can be offered under an elevated-temperature heat cycle as explained above. Therefore, it is invention with industrial high value, such as being able to promote efficient-izing, lightweight-izing, etc. of a semi-conductor, a liquid crystal manufacturing installation, etc., and doing so effectiveness, such as enabling efficient production of the semi-conductor of high performance, or liquid crystal manufacture, which is the application of aluminum ingredient concerning this invention.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] It has the porous layer which has said a majority of pores, and a barrier layer without pore, and is the porous layer 4. Surely the anodic oxide film made small as the diameter of a cel of the diameter of pore by the side of a front face can be carried out is excellent in the corrosion resistance over said gas and plasma. however, the manufacture conditions of a semi-conductor or liquid crystal -- the latest efficient-izing and enlargement -- a very severe thing -- becoming -- **** -- gas, plasma condition nearby high concentration, and high density -- it has elevated-temperature-ized. therefore, the reaction container (chamber) a configuration member and the use member in the interior -- receiving -- halogens, such as Cl, and F, Br, O and N, H, B, S, and C etc. -- the corrosion resistance over corrosive gas and the corrosive plasma containing an element is required, and the demand is severer recent years still. On the other hand, in the anodic oxide film obtained by said anodizing, it cannot reply to the corrosion resistance demand to said this gas or plasma that are severe.

[0009] Moreover, heat-resistant demand to the charge of manufacturing installation material of the target semi-conductor [this invention] in one side (technical problem) It is severer recent years still. Especially, in the member for manufacturing installations of a semi-conductor, it is under the severe operating environment of receiving many heat cycles in a pyrosphere while in use according to the process conditions of manufacture of a semi-conductor as described above. For this reason, under this elevated-temperature heat cycle, a crack occurs in an anodic oxide film, a corrosion component trespasses upon the bottom of the corrosive environment of said gas and plasma from the crack of this anodic oxide film, and the anodic oxide film obtained by said anodizing has a problem of making aluminum alloy which is a base material corrode. Therefore, in order to fill the heat-resistant demand to the charge of manufacturing installation material of these semi-conductors, it is necessary to improve the heat-resistant crack nature which prevented crack generating of the anodic oxide film under an elevated-temperature heat cycle.

[0010] This invention is made paying attention to such a situation, under an elevated-temperature heat cycle, moreover, even if the purpose is under the corrosive environment of said gas and plasma, a crack does not occur in an anodic oxide film, but it tends to offer aluminum ingredients aluminum alloy which prepared the anodic oxide film which is moreover excellent with the corrosion resistance over said gas and plasma, i.e., for vacuum housings etc.

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MEANS

[Means for Solving the Problem] In order to attain this purpose, the summary of this invention It is aluminum ingredient with which the anodic oxide film which has the porous layer which has pore, and a barrier layer without pore as an aluminum ingredient excellent in heat-resistant crack nature and corrosion resistance was formed in the front face. As compared with aluminum alloy base material side, the front-face side of an anodic oxide film is made small for the diameter of pore of said porous layer. Further from an anodic oxide film front face in 5% or more of depth part of the thickness of film And the part more than 20 % is boehmite and/at the rate of the volume to a coat layer. Or it is forming pseudo-boehmite.

[0012] It is the front face or the whole of anodic oxidation coatings Boehmite and/Or sealing with pseudo-boehmite itself is common knowledge. That is, aluminum alloy ingredient which prepared the anodic oxide film is processed with warm water, pressurization water, a steam, etc., and it is common knowledge about the front face or the whole of an anodic oxide film boehmite-ization or to form pseudo-boehmite, to seal the pore of the porous layer of an anodic oxide film, and to raise the corrosion resistance of an anodic oxide film more.

[0013] However, the purpose of well-known sealing is conventionally [these] for raising more the corrosion resistance under general corrosive environment under the ambient atmosphere in which humidity thru/or salts, etc. of aluminum alloy ingredient which prepared the anodic oxide film exists, or atmospheric air. Therefore, it is not the corrosion resistance improvement purpose to the crack prevention of an anodic oxide film, gas, or the plasma of aluminum alloy ingredient which moreover prepared the anodic oxide film under the corrosive environment of said gas and plasma under an elevated-temperature heat cycle like this invention.

[0014] And aluminum alloy ingredient which prepared the anodic oxide film made into the object of sealing is not aimed at the thing of the structure of anodic oxide coating of the inclination structure to which the path of the pore of the porous layer of an anodic oxide film targetted [a diameter of pore of a porous layer like this invention] small the thing of the usual structure of anodic oxide coating which becomes the same for the front-face side of an anodic oxide film as compared with aluminum alloy base material side by front-face [of an anodic oxide film], and aluminum alloy base material side thru/or multilayer structure, either.

[0015] and -- a purpose [seal / the pore of a porous layer / well-known sealing / conventionally / these / completely] -- carrying out -- the anodic-oxidation-coatings coat whole -- boehmite-izing -- or pseudo-boehmite is formed. For this reason, boehmite-izing or the volume of an anodic oxide film formed into pseudo-boehmite changes a lot. (expansion) It carries out. Therefore, depending on the operating environment and conditions of aluminum ingredient, a crack occurs in the depth direction of an anodic oxide film, and the heat-resistant crack nature of an anodic oxide film and corrosion resistance deteriorate on the contrary. [like / said vacuum housing or for process reaction containers] Especially, moreover, the inclination does not bear use remarkably under the corrosive environment of said gas or plasma under said elevated-temperature heat cycle.

[0016] In order to prevent the crack accompanying said volume change of the anodic oxide film in such conventional sealing, even if it is under the corrosive environment of said gas and plasma, moreover, the thermal stress difference between the anodic oxide film produced in this environment and aluminum alloy base material and the stress generated inside an anodic oxide film are eased under said elevated-temperature heat cycle. (buffer) It is necessary to carry out. For this reason, in this invention, the front-face side of an anodic oxide film is made small for the diameter of pore of said porous layer as compared with aluminum alloy base material side. (it enlarging and making it become by aluminum alloy base material side small by the front-face side of an anodic oxide film) An anodic oxide film is made into multilayer structure or inclination structure. And let boehmite-izing of anodic oxidation coatings, or the amount of formation of pseudo-boehmite be the specific range from crack prevention of anodic oxidation coatings and a corrosion-

resistant viewpoint.

[0017] Namely, preferably, under said elevated-temperature heat cycle, although it carries out to more than the initial complement for sealing pore in order to raise corrosion resistance even if boehmite-izing of anodic oxidation coatings or the amount of formation of pseudo-boehmite in this invention is under the corrosive environment of said gas and plasma, moreover It carries out to below an amount that the crack of an anodic oxide film produces with the thermal stress difference between the anodic oxide film produced in this environment, and aluminum alloy base material, and extent of the stress generated inside an anodic oxide film. Moreover, it is the fundamental views of this invention extent of the stress which generates the diameter of pore of said porous layer inside the thermal stress difference between the anodic oxide film which also produces extent which makes small the front-face side of an anodic oxide film as compared with aluminum alloy base material side in this environment, and aluminum alloy base material, and an anodic oxide film, and that these shall be eased and the effectiveness that the crack of an anodic oxide film can be prevented shall be attained substantially.

[0018] In addition, although sealing of the pore may be carried out as a result by formation of the boehmite of this invention, or pseudo-boehmite, at this invention, it is extent of the sealing. (perfect sealing and half-sealing) It is not a problem and the amount of the boehmite formed or pseudo-boehmite governs the heat-resistant crack nature and corrosion resistance which are made into the purpose to the last.

[0019]

[Embodiment of the Invention] It is drawing 1 about the structure of anodic oxide coating of this invention based on this fundamental view. It is shown typically. this drawing 1 as being shown -- anodic oxide film A of this invention Base material aluminum alloy 1 a front face -- pore 3 having -- aluminum alloy 1 Cel 2 which grows in the depth direction from -- becoming porous layer 4 Barrier layer 5 without pore from -- it becomes. And pore 3 The diameter W1 of pore by the side of the front face of an anodic oxide film is made smaller than the diameter W2 of pore by the side of aluminum alloy base material, and it does not matter even if change of this diameter of pore has the continuous change section like pore 3a in the arbitration section of the depth direction, and whether it has the discontinuous change section like pore 3b in the arbitration section of the depth direction or these are intermingled. In this invention, the case of pore 3a in which the diameter of pore has the continuous change section is called said inclination structure, and the case of pore 3b in which the diameter of pore has the discontinuous change section is called said multilayer structure. In addition, drawing 2 described above in the usual anodic oxide film It is pore 3 like. A path becomes the same at front-face [of an anodic oxide film], and aluminum alloy base material side.

[0020] and such anodic oxidation coatings A setting -- further -- bainite and/Or pseudo-bainite 6 an anodic-oxidation-coatings front face to 5% or more of the thickness of film -- desirable -- 90% or less of coat depth (thickness) the rate [as opposed to a coat layer to the part of 1] of the volume -- 20% the above -- desirable -- 80% it contains below -- making -- the surface layer of anodic oxidation coatings -- partial -- boehmite-izing -- or pseudo-boehmite is made to form boehmite-izing or in this case, making pseudo-boehmite form -- mainly -- porous layer 4 of anodic oxidation coatings it is -- although -- it may result in a barrier layer depending on coat conditions

[0021] The boehmite or pseudo-boehmite said by this invention is the hydration oxide of aluminum, is expressed with general formula and $\text{Al}_2\text{O}_3 \cdot \text{XH}_2\text{O}$, and says the hydration oxide of aluminum generated by the hydration reaction of the oxide of aluminum of an anodic oxide film by hydration processing. And said X Generally the value is called boehmite or pseudo-boehmite in the thing of about 1-1.9.

[0022] Measurement of the amount of the boehmite in these anodic oxidation coatings or pseudo-boehmite is 2. It is difficult when the boehmite or pseudo-boehmite currently especially formed only by the gestalt-observation by the scanning electron microscope of 10,000 times or more is a detailed crystal. therefore, measurement of the amount of boehmite or pseudo-boehmite -- X Line diffraction and X Linear-light electron spectroscopy analysis (XPS) and infrared spectral-analysis method (FT-IR) etc. -- by using, it can measure correctly. For example, $\text{AlO} \leftrightarrow \text{H}$ which will be accepted in the 3000-3700 cm^{-1} neighborhood if the case of FT-IR is taken for an example The absorption spectrum by stretching vibration, And by accepting any one of the absorption spectrums by the stretching vibration of $\text{aluminum} \leftrightarrow \text{OH}$ accepted in the 1050-1100 cm^{-1} neighborhood Existence of the hydration oxide film of aluminum is checked and they are the discernment from the amorphous tissue of the original anodic oxide film, and the depth of an anodic oxide film from the reinforcement of those spectrums. (thickness) Quantitive analysis of a direction is possible. Moreover, X In line diffraction, quantitive analysis is possible similarly from the X diffraction peak intensity of aluminum-OOH .

[0023] Next, the quantitative conditions in this invention of boehmite-izing or the formation of pseudo-

boehmite are explained. in order [first,] to raise the corrosion resistance under the corrosive environment of said gas and plasma in this invention -- the boehmite of anodic oxidation coatings, or the amount of pseudo-boehmite formation -- boehmite or pseudo-boehmite -- 5% or more of depth of an anodic-oxidation-coatings front face to the thickness of film -- desirable -- 40% the above depth -- and it is made to contain more than 50 % preferably more than 20 % at the rate of the volume to a coat layer

[0024] In addition, function of boehmite and pseudo-boehmite (effectiveness) It may be the same, and as for boehmite or pseudo-boehmite, it may be independent to make it form thru/or contain in anodic oxidation coatings, or it may be mixing.

[0025] If the thickness of the anodic oxide film which boehmite or pseudo-boehmite contains is less than 5% of the thickness of film, the corrosion resistance over gas or the plasma will become less enough. Moreover, the content of the boehmite or pseudo-boehmite of the surface part of anodic oxidation coatings concerned is 20% at the rate of the volume to a coat layer. The corrosion resistance over gas or the plasma becomes less enough also in the following.

[0026] On the other hand, with the stress which is produced in this invention under said elevated-temperature heat cycle and the corrosive environment of gas or the plasma and which is generated inside an anodic oxide film, and the thermal stress difference between aluminum alloy base materials and an anodic oxide film Thickness of the anodic oxidation coatings which boehmite or pseudo-boehmite contains in order to prevent that a crack arises in anodic oxidation coatings (depth) An upper limit 90% of the thickness of film It is 80% at the rate [as opposed to a coat layer for the upper limit of the content of the boehmite or pseudo-boehmite of the surface parts of the following and anodic oxidation coatings concerned] of the volume. Considering as the following is desirable.

[0027] It can prevent fundamentally that it is eased by multilayer-structure-izing and inclination structuring of an anodic oxide film which are one of the requirements for this invention and which make small the front-face side of an anodic oxide film for the diameter of pore as compared with aluminum alloy base material side, and a crack produces said thermal stress difference and stress in an anodic oxide film by them. However, in order to prevent more certainly the crack of anodic oxidation coatings at the time of the operating environment of aluminum alloy ingredient becoming severer, the conditions of the desirable upper limit of boehmite-izing of said anodic oxidation coatings or the formation of pseudo-boehmite are needed.

[0028] That is, the thickness of the anodic oxide film which boehmite or pseudo-boehmite contains is 90% of the thickness of film. If it exceeds Moreover, the content of the boehmite or pseudo-boehmite of the surface part of anodic oxidation coatings concerned is 80% at the rate of the volume to a coat layer. If it exceeds said conventional sealing -- the same -- anodic oxidation coatings -- substantial -- the coat whole -- said boehmite-izing -- or pseudo-boehmite is formed -- ***** -- change of the volume of anodic oxidation coatings (expansion) It becomes larger. For this reason, in case it becomes easy to generate a crack in the depth direction of an anodic oxide film and the operating environment of said aluminum alloy ingredient becomes severer in it, it is because the crack nature of an anodic oxide film and corrosion resistance may result in deteriorating on the contrary.

[0029] Next, in order to prevent the crack accompanying the volume change of an anodic oxide film in the anodic oxide film which has a porous layer and a barrier layer as describe above, the anodic oxide film itself eases the stress moreover generate also under the corrosive environment of said gas and plasma inside the thermal stress difference between the anodic oxide film produce in this environment, and aluminum alloy base material, and an anodic oxide film under said elevated temperature heat cycle. (buffer) It is needed that it is the make structure. As an improvement of the structure of anodic oxide coating for this itself, it has chosen making small the diameter of pore by the side of the front face of a porous layer as compared with aluminum alloy base material side by this invention. Said thermal stress difference or stress cannot be eased in the anodic oxide film which has a formal porous layer and a formal barrier layer as other modes conventionally which makes the diameter of pore the same at front-face [of a porous layer], and aluminum alloy base material side, or the anodic oxide film which has conversely a porous layer which enlarges the diameter of pore by the side of the front face of a porous layer as compared with aluminum alloy base material side, and a barrier layer. Moreover, since it is connected with degrading basic properties, such as plasma-proof nature, it is not appropriate to enlarge the diameter of pore by the side of a front face as compared with aluminum alloy base material side.

[0030] Thus, in this invention, an anodic oxide film is made into layer structure or inclination structure so that the diameter of pore may be small enlarged by aluminum alloy base material side by the front-face side and it may become for relaxation of said thermal stress difference and stress. More specifically in the range of the usual anodic oxide film processing, the diameter of pore by the side of aluminum alloy base material Since it becomes the range of 5 - 100 nm, it corresponds to this, and it is a diameter of pore by the side of a

front face 1/2 - 1/3 of the diameter of pore by the side of a base material It is desirable to make it small the following. In addition, whether it has the continuous change section in the arbitration section of the depth direction or change of the diameter of pore of said porous layer has the discontinuous change section in the arbitration section of the depth direction, it is not cared about.

[0031] Moreover, also by thickening said barrier layer side of anodic oxidation coatings, said stress is eased, it is effective in preventing the crack accompanying the volume change of anodic oxidation coatings, and corrosion resistance can also be raised further. Therefore, it is desirable to set thickness of a barrier layer to 30nm or more. Thus, the crack of a coat and exfoliation which can ease the stress and the volume change which are produced when corrosive gas and plasma, such as anodic oxidation coatings and a halogen, contact, consequently serve as an origin of corrosion or damage during use are controlled, and controlling the thickness of the barrier layer of anodic oxidation coatings also demonstrates aluminum alloy front face and the outstanding adhesion.

[0032] The thickness of the whole anodic oxide film containing a porous layer and a barrier layer is 0.1 in order to demonstrate said outstanding corrosion resistance of an anodic oxide film. mum The above is desirable and it is 1. mum It is more desirable if it is above. However, if the thickness of an anodic oxide film is too thick, since a crack is produced under the effect of internal stress, surface covering will become inadequate, or exfoliation of a coat will be caused and the coat engine performance will be checked on the contrary, the thickness of a coat is 200. mum It is 100 preferably hereafter. mum It is good to consider as the following.

[0033] Furthermore, they are C, S, N, P, F, and B in an anodic oxide film as other modes with desirable this invention. 1 chosen from inside A kind or 2 By including the element beyond a seed, the plasma-proof nature of the anodic oxide film itself can be raised, and the elevated-temperature heat cycle of aluminum alloy base material and an anodic oxide film and the adhesion under a high-temperature-corrosion environment can be improved. For that, it is at least 1 of these elements. A seed needs to contain 0.1% or more. For example, an anodic oxide film is C of said elements. 1 If only a seed is contained 0.1% or more, other element contents will be 0.01 less than 0.1%%. It is C even when it is content of the minute amount which is extent. The element of the minute amount content demonstrates the improvement effectiveness in adhesion.

[0034] Subsequently, the approach of the anodization thru/or boehmite-izing in this invention, or pseudo-boehmite-ized processing is explained. First, boehmite-izing or the approach itself formed into pseudo-boehmite can adopt approaches, such as well-known hydration processing, for anodic oxidation coatings partially. namely, the thing which aluminum alloy ingredient which prepared the anodic oxide film is put to the ambient atmosphere of immersion or pressurization water pressure, and a water vapor pressure into warm water at the temperature of 70 - 270 ** with warm water, pressurization water, a steam, etc. -- processing -- the front face of an anodic oxide film -- boehmite-izing -- or pseudo-boehmite is formed. However, it is as having described above that it is necessary to make this boehmite-izing or pseudo-boehmite-ization into said specific condition range.

[0035] Next, the anodizing approach in this invention is explained. First, while forming the anodic oxide film which has said porous layer and a barrier layer without pore, it is the porous layer 4 further. While making small the diameter of pore by the side of a front face, it is the porous layer 4. The diameter of pore by the side of a base material is enlarged, and it is the barrier layer 5. As an approach of forming the thickened anodic oxide film, the anodic oxidation approach indicated by said JP,8-144088,A and JP,8-260196,A can be used.

[0036] More specifically, it is 50V about the initial voltage of anodic oxidation like said JP,8-144088,A. While considering as the following, it is 50V about the telophase electrical potential difference of anodic oxidation. It may be made high with the above and the anodic oxide film which has said porous layer and a barrier layer without pore may be formed. Moreover, they are solutions, such as a sulfuric acid, phosphoric acid, and a chromic acid, first like JP,8-260196,A. (electrolytic solution) With the electrolytic voltage of 5 - 200V Porous mold anodizing for the porous layer coat formation which has pore is performed. Subsequently Solutions, such as a way acid system, a phosphoric acid system, a phthalic-acid system, an adipic-acid system, a carbonic acid system, a citric-acid system, and a tartaric-acid system (electrolytic solution) ***** is also good in non-porous mold anodizing for the barrier layer coat formation which does not have pore by the electrolytic voltage of 60-500V.

[0037] Furthermore, in order to make the diameter of pore by the side of the front face of a porous layer smaller than a base material side, it sets at an anodic oxidation process, and it is 10-50V about electrolytic voltage. Or 10-80V When changing the diameter of pore continuously, and change of this electrolytic voltage changes the diameter of pore in discontinuous continuously, change of this electrolytic voltage is

changed [while making it change in the range,] intermittently.

[0038] Moreover, C which is the desirable mode of above mentioned this invention, S, N, P, F, and B The content to the anodic oxide film of an element is 1 chosen from acids, such as oxalic acid, a sulfuric acid, a way acid, phosphoric acid, a phthalic acid, and formic acid. A kind or 2 The anodic oxidation which used the water solution or mixed water solution beyond a seed as the electrolytic solution performs. This approach itself is concretely indicated by said JP,8-193295,A. namely, -- if for example, an oxalic acid goat acid is used as an anodizing solution -- aluminum₄C₃, aluminum₂C₅, HCOOH, and 2 (COOH) etc. -- C the included compound introduces to an anodic oxide film -- having -- as a result -- C It contains to an anodic oxide film. That is, at this invention, they are C, S, N, P, F, and B. Content to the anodic oxide film of an element may be performed in the ion of these elements thru/or the form of a compound.

[0039] for example, S the case where it contains to an anodic oxide film -- a sulfuric-acid water solution thru/or a sulfuric acid, and aluminum₂(SO₄)₃ etc. -- anodic oxidation, with the water solution added in said acid solution -- H₂SO₄, H₂SO₃, aluminum₂(SO₄)₃, and aluminum (HSO₄)₃ etc. -- S The included compound is introduced to an anodic oxide film. Moreover, N They are N, such as HNO₃ and aluminum (NO₃)₃, by adding HNO₃ and aluminum(NO₃)₃ grade in said acid solution, in containing to an anodic oxide film. The included compound is introduced to an anodic oxide film, and it is N as a result. It contains to an anodic oxide film. furthermore, P the case where it contains to an anodic oxide film -- anodic oxidation, with phosphoric acid thru/or a phosphoric acid salt water solution -- H₃PO₄ and H₃ -- PHO₃ and AlPO₄ ***** -- P It contains to an anodic oxide film. Moreover, they are H₃PO₄, H₃PO₃, and AlPO₄ to other acid solutions. You may add and anodize. F It is F by adding HF in said acid solution, in containing to *****. It contains to an anodic oxide film. furthermore, B the case where it contains to an anodic oxide film -- 2B (NH₃)₄O₇ and H₃BO₃ etc. -- adding in said acid solution -- B It contains to an anodic oxide film as 2B (NH₃)₄O₇ or B-2 O₃.

[0040] In addition, the anodizing conditions which introduce these elements into a coat are C, S, N, P, F, and B. At least 1 of the elements Although a seed is decided by the conditions contained 0.1% or more Under the present circumstances, C, S, N, P, F, and B Since the amount of installation to an anodic oxide film changes also with anodic oxidation conditions, such as concentration of the compound of a presentation and organization of aluminum alloy and said acid thru/or these acids, water-solution temperature, stirring conditions, and current conditions, this condition is adjusted suitably and it performs it. The electrolytic solution which contains 1 or more g/l of said oxalic acid from the point which can control the electrolytic voltage of anodic oxidation in the large range is desirable. And the electrolytic voltage of anodic oxidation is chosen from the range of 5 -200V. On the other hand, since aluminum ingredient of this invention makes the main application charges of vacuum housing material, such as a semi-conductor and a manufacturing installation of liquid crystal, it eliminates it that the element with which the electrolytic solution of anodic oxidation leads to contamination of products, such as a semi-conductor and liquid crystal, is included as much as possible.

[0041] furthermore, the JIS 3003aluminum alloy which contains Mn:1.0-1.5%-Cu:0.05-0.20% etc. especially about aluminum alloy used for this invention, and Mg:2.2-2.8%-Cr:0.15-0.35% etc. -- the JIS 6061aluminum alloy containing the included JIS 5052aluminum alloy, Cu:0.10 -0.40%-Mg:0.5-1.5%-Cr:0.04-0.35%-Si:0.5-1.5%, etc. is illustrated. aluminum alloys in this invention are the demand characteristics of each vacuum housings, such as a semi-conductor and a manufacturing installation of liquid crystal. s (reinforcement, workability, thermal resistance, etc.) It responds and is JIS of said JIS 3003, 5052, 6061 grades, or others. A specification aluminum alloy can be used choosing it suitably. Of course, aluminum alloy which changed the alloy presentation of these existing is also usable.

[Translation done.]

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EXAMPLE

[Example] Anodizing is performed to a JIS 6061 aluminum alloy plate, and it is Table 1. The shown anodic oxide film was prepared. Anodizing was the electrolytic solution which carries out 30-200 g/l content of the acid which is mentioned later, anodized electrolytic voltage in 5 -150V, and prepared the anodic oxide film which has a porous layer and a barrier layer without pore. Among this, example No. of invention 1-7, example No. of comparison 10, and 11 In order to make the diameter of pore by the side of the front face of a porous layer smaller than a base material side, it is 10-50V about electrolytic voltage. Or 10-80V While making it change in the range, when changing the diameter of pore continuously When change of this electrolytic voltage changed the diameter of pore in discontinuous continuously, change of this electrolytic voltage was changed intermittently.

[0043] Consequently, 2 The structure of anodic oxide coating checked with the 10,000 times as many scanning electron microscope as this the anodic oxide film which has a porous layer and a barrier layer without pore -- setting -- (**) Drawing 2 Example which made the diameter of pore of a porous layer the same as the depth direction like (8 example No. of comparison. of Table 1 9) (b) The diameter of pore by the side of the front face of a porous layer is made smaller than a base material side like pore 3a of drawing 1. example for which the diameter of pore has the continuous change section in the arbitration section (example No. of invention. of Table 1 -- 2 and 5 --) 6 Example No. of comparison 11 (Ha) Drawing 1 The diameter of pore by the side of the front face of a porous layer is made smaller than a base material side like like pore 3b. The diameter of pore is Table 1 in the arbitration section. 3 indicated It has the gradual discontinuous change section. (the porous layer from which the diameter of pore differs is 3 it has layer structure) Example (example No. of invention. of Table 1 1, 3, 4, 7, example No. of comparison. 10) 3 It had become a class. The example of invention and the example of a comparison of the thickness of the barrier layer of anodic oxidation coatings were 50nm or more altogether.

[0044] Moreover, content of each element to an anodic oxide film is C. Content is oxalic acid and P. Content is phosphoric acid and S. Content performed the sulfuric acid or the sulfurous acid as the electrolytic solution respectively. And when making these elements compound and contain, according to the combination of an element, the electrolytic solution mixed respectively performed said acid. It is more specifically C. Content the electrolytic solution Oxalic acid (30 g/l), C S Content is oxalic acid (30 g/l) about the electrolytic solution. A mixed acid with a sulfuric acid (5 g/l), C S Content is oxalic acid (30 g/l) about the electrolytic solution. A mixed acid with a sulfuric acid (3 g/l), and P and S Content is phosphoric acid (60 g/l) about the electrolytic solution. Sulfuric acid (60 g/l) It considers as a mixed acid. The loadings of an acid are adjusted, each element content is adjusted, and it is Table 1. The specified quantity of each shown element was made to contain to an anodic oxide film.

[0045] Further aluminum alloy ingredient which prepared the anodic oxide film with a steam and at the temperature of 180 ** 2 The thickness of the anodic oxide film which performs hydration processing put to the ambient atmosphere of the water vapor pressure of a toll, and boehmite or pseudo-boehmite contains 5% or more of the thickness of film, and 90% the rate [as opposed to a coat layer for the content of the boehmite or pseudo-boehmite of the surface parts of the following and anodic oxidation coatings concerned] of the volume -- 20% the above -- 80% the following -- it should carry out -- boehmite-izing -- or pseudo-boehmite was formed. The amount of these boehmite-izing or the formation of pseudo-boehmite is also Table 1. It is shown.

[0046] In addition, at this example, the amount of boehmite-izing of anodic oxidation coatings or the formation of pseudo-boehmite is X. Line diffraction and X Linear-light electron spectroscopy analysis (XPS) Concomitant use performed discernment and quantitative analysis with aluminum-O which is the tissue of the original anodic oxidation coatings, aluminum-OH, and aluminum-O-OH. That is, it is thickness about the anodic oxidation coatings of the example of invention, and the example of a comparison. (the depth

direction) Thickness from the coat front face of the anodic oxidation coatings which carry out quantitative analysis and which boehmite or pseudo-boehmite contains (rate % to the thickness of the depth and the whole coat) And content of boehmite or pseudo-boehmite (rate of volume % to a coat layer) Table 1 It is shown quantitatively.

[0047] And the line evaluated [aluminum alloy plate which prepared these boehmite-izing or anodic oxide films which were formed into pseudo-boehmite] the crack nature of the anodic oxide film under an elevated-temperature heat cycle and corrosive environment, gas, and plasma corrosion resistance for ** heatproof crack sex test, the halogen-proof [**] gas corrosive trial, and the plasma-proof [**] corrosive trial respectively. These results are also Table 1. It is shown.

[0048] In addition, the concrete conditions of ** heatproof crack sex test of the boehmite-izing or the anodic oxide film formed into pseudo-boehmite under an elevated-temperature heat cycle and a high-temperature-corrosion environment are heating from a room temperature to 250 ** 5 After cycle *****, the surface situation of an anodic oxide film was observed under the microscope, and the generating situation of the crack to the depth direction of a coat was investigated. Consequently, that in which ** and a macro-crack have generated that in which O and a minute crack have generated the thing without generating of a crack was made into x.

[0049] Moreover, the concrete conditions of a halogen-proof [**] gas corrosive trial It doubles with the severer conditions of the actual service conditions of semiconductor fabrication machines and equipment. 300 ** is Cl₂ 5% about the test piece of aluminum alloy plate which prepared said coat. It is 120 to content Ar gas. The trial exposed between parts is performed. Exfoliation situation of an anodic oxide film at the time of sticking and removing a tape all over the front face of the test piece after exposure (stripped plane product) It investigates. O and a stripped plane product are 25% of test piece surface area about a thing without exfoliation. ** and a stripped plane product are as follows 26% of test piece surface area. What has exceeded and spread was evaluated as x.

[0050] Furthermore, the concrete conditions of a plasma-proof [**] corrosive trial It doubles with the severer conditions of the actual service conditions in semiconductor fabrication machines and equipment. To the test piece of aluminum alloy plate which prepared said coat, it is the cooling 5 for [BC13 plasma exposure] 10 minutes. It is between parts 6 The amount of etching on the front face of anodic oxidation coatings after ***** is measured under a microscope. The amount of etching is 1. O and the amount of etching are as follows [a micron] 1-3. ** and the amount of etching are the thing of a micron 3 The thing exceeding a micron was evaluated as x.

[0051] Table 1 since -- a clear passage -- anodic oxidation coatings -- (1) It has the porous layer which has pore, and a barrier layer without pore. And (2) In the diameter of pore of said porous layer, are small at the front-face side of an anodic oxide film. And it comes to enlarge by aluminum alloy base material side, and is (3) further. The thickness from the coat front face which boehmite or pseudo-boehmite contains 5% or more, And (4) The content of boehmite or pseudo-boehmite is 20%. With the anodic oxide film which consists of the above (5) -- C, S, N, P, F, and B Example No. of invention 1-7 which formed the content anodic oxide film for the element any 0.1% or more The result of having excelled also in ** heatproof crack sex test, a halogen-proof [**] gas corrosive trial, a plasma-proof [**] corrosive trial, and ***** is obtained. [and] however, example No. of invention. -- 3 and 7 There are comparatively few amounts of boehmite or the formation of pseudo-boehmite, and a halogen gas corrosive is comparatively inferior as compared with other examples of invention. Therefore, if the requirements and the desirable requirements for this invention are satisfied, it turns out that it excels in gas corrosion resistance or plasma corrosion resistance, and excels also in the heat-resistant crack nature of an anodic oxide film which guarantees this fundamentally.

[0052] on the other hand, table 1 from -- a clear passage -- example No. of comparison. -- 8 and 9 although other requirements for this invention are satisfied -- the diameter of pore of an anodic oxide film -- a front-face side and a base material side -- the same -- the above (2) It is lacking in requirements, and the diameter of pore is not made small by the front-face side of an anodic oxide film, but an anodic oxide film is the monolayer structure where it does not have a multilayer thru/or inclination structure. moreover, example No. of comparison. -- 10 and 11 -- the each above (3) requirements -- lacking -- boehmite or pseudo-boehmite -- said less than 5% of anodic oxide film thickness -- there is nothing -- example No. of comparison 11 further -- the above (4) It is lacking and under 20 % of a coat layer is not making requirements contain. therefore, example No. of comparison. -- 8 and 9 The heat-resistant crack nature of an anodic oxide film and a plasma-proof corrosive are inferior, and example No. of comparison 10 and 11 are inferior to the example of invention in a plasma-proof corrosive and a halogen-proof gas corrosive. moreover, example No. of comparison. -- 8 and 9 It is also thought that that the amount of formation of boehmite or pseudo-boehmite is over 80% is the cause to which it reduces heat-resistant crack nature and a plasma-proof corrosive.

[0053] aluminum ingredient concerning this invention a passage clear from this example Moreover under an elevated-temperature heat cycle, it is under the corrosive environment of said gas and plasma. It excels as the member used inside a vacuum housing, a process reaction container, or these containers, or an object for ingredients. inside -- especially -- CVD PVD etc. -- it turns out chemical or that it excels as the member used inside containers, such as a manufacturing installation of semi-conductors, such as a physical vacuum evaporation system or a dry etching system, or liquid crystal, or these containers, or an object for ingredients. Furthermore, aluminum ingredient concerning this invention is applicable to a building material, an automobile ingredient, etc. also for applications other than these.

[0054]

[Table 1]

略号	区分	陽 極 酸 化 皮 膜						①耐熱 割れ性 試験	②HCl 腐食 試験	③F ₂ /H ₂ O 腐食 試験
		ポア径		皮膜含有元素 (wt%)	皮膜の 総膜厚 (μm)	ペーナイト/擬ペーナイト 化条件				
		ポア径(mm) 表面側/基材側	孔径の 変化			皮膜含 有物	厚さ×含有量 (%)			
1	発明例	20 / 40 : 80	非連続	C:1.0、S:0.3	50	①	20 × 80	○	○	○
2	発明例	35 / 95	連続	C:1.5	15	①+②	60 × 70	○	○	○
3	発明例	35 / 45 : 95	非連続	P:1.0、S:0.3	5	①+②	40 × 30	○	△	○
4	発明例	15 / 30 : 70	非連続	C:1.2、S:0.5	75	①	30 × 50	○	○	○
5	発明例	10 / 15 : 25	非連続	S:1.5	75	①+②	80 × 80	○	○	○
6	発明例	30 / 100	連続	C:1.5	10	①+②	60 × 60	○	○	○
7	発明例	20 / 45 : 60	非連続	C:1.2、S:0.5	45	②	20 × 25	○	△	○
8	比較例	25 / 25	無し	S:0.3	75	①	20 × 85	×	○	×
9	比較例	80 / 80	無し	C:1.5、S:0.3	50	①+②	80 × 95	×	○	×
10	比較例	35 / 45 : 95	非連続	P:1.0、S:0.3	5	①+②	20 × 3	○	×	△
11	比較例	10 / 25	連続	S:1.5	75	①	1 × 3	○	×	△

* 上記皮膜含有物において、①はペーナイト、②は擬ペーナイトで、①+②はこれらの混合物

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the explanatory view showing typically the outline structure of this invention anodic oxide film.

[Drawing 2] It is the explanatory view showing the outline structure of the conventional anodic oxide film typically.

[Description of Notations]

A B : anodic oxide film

1: aluminum alloy base material 2 : Cell wall 3: Pore

4: Porous layer 5 : Barrier layer 6: Boehmite - pseudo-boehmite

7: Front-face side of the anodic oxide film of pore 8: aluminum alloy base material side of pore

[Translation done.]